105409

APPENDIX B

ANALYTICAL METHODS

300524

ALKALINITY

Method 310.1 (Titrimetric, pH 4.5)

STORET NO. 00410

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.
   - 1.3 Automated titrimetric analysis is equivalent.
2. Summary of Method
   - 2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.
3. Comments
   - 3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
   - 3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.
   - 3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:
     Annual Book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, (1976).
   - 3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.
4. Apparatus
   - 4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ±2° C.
   - 4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and buret.
   - 4.3 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.
   - 4.4 Burets, Pyrex 50, 25 and 10 ml.
5. Reagents
   - 5.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ±0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

Approved for NPDES
Issued 1971
Editorial revision 1978

300525

Designation: D 421 – 85

Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[1]

This standard is issued under the fixed designation D 421; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the dry preparation of soil samples as received from the field for particle-size analysis and the determination of the soil constants.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 2217 Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

3. Significance and Use

3.1 This practice can be used to prepare samples for particle-size and plasticity tests where it is desired to determine test values on air-dried samples, or where it is known that air drying does not have an effect on test results relative to samples prepared in accordance with Practice D 2217.

4. Apparatus

4.1 *Balance*, sensitive to 0.1 g.

4.2 *Mortar and Rubber-Covered Pestle*, suitable for breaking up the aggregations of soil particles.

4.3 *Sieves*—A series of sieves, of square mesh woven wire cloth, conforming to Specification E 11. The sieves required are as follows:

No. 4 (4.75-mm)
No. 10 (2.00-mm)
No. 40 (425-μm)

4.4 *Sampler*—A riffle sampler or sample splitter, for quartering the samples.

5. Sampling

5.1 Expose the soil sample as received from the field to the air at room temperature until dried thoroughly. Break up the aggregations thoroughly in the mortar with a rubber-covered pestle. Select a representative sample of the amount required to perform the desired tests by the method of quartering or by the use of a sampler. The amounts of material required to perform the individual tests are as follows:

5.1.1 *Particle-Size Analysis*—For the particle-size analysis, material passing a No. 10 (2.00-mm) sieve is required in amounts equal to 115 g of sandy soils and 65 g of either silt or clay soils.

5.1.2 *Tests for Soil Constants*—For the tests for soil constants, material passing the No. 40 (425-μm) sieve is required in total amount of 220 g, allocated as follows:

Test	Grams
Liquid limit	100
Plastic limit	15
Centrifuge moisture equivalent	10
Volumetric shrinkage	30
Check tests	65

6. Preparation of Test Sample

6.1 Select that portion of the air-dried sample selected for purpose of tests and record the mass as the mass of the total test sample uncorrected for hygroscopic moisture. Separate the test sample by sieving with a No. 10 (2.00-mm) sieve. Grind that fraction retained on the No. 10 sieve in a mortar with a rubber-covered pestle until the aggregations of soil particles are broken up into the separate grains. Then separate the ground soil into two fractions by sieving with a No. 10 sieve.

6.2 Wash that fraction retained after the second sieving free of all fine material, dry, and weigh. Record this mass as the mass of coarse material. Sieve the coarse material, after being washed and dried, on the No. 4 (4.75-mm) sieve and record the mass retained on the No. 4 sieve.

7. Test Sample for Particle-Size Analysis

7.1 Thoroughly mix together the fractions passing the No 10 (2.00-mm) sieve in both sieving operations, and by the method of quartering or the use of a sampler, select a portion weighing approximately 115 g for sandy soils and approximately 65 g for silt and clay soil for particle-size analysis.

8. Test Sample for Soil Constants

8.1 Separate the remaining portion of the material passing the No. 10 (2.00-mm) sieve into two parts by means of a No 40 (425-μm) sieve. Discard the fraction retained on the No

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[1] This practice is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved July 26, 1985. Published September 1985. Originally published as D 421 – 35 T. Last previous edition D 421 – 58 (1978)[ε1].

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

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40 sieve. Use the fraction passing the No. 40 sieve for the determination of the soil constants.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

300527

Designation: D 422 – 63 (Reapproved 1972)[ε1]

Standard Method for Particle-Size Analysis of Soils[1]

This standard is issued under the fixed designation D 422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[ε1] NOTE—Section 2 was added editorially and subsequent sections renumbered in July 1984.

1. Scope

1.1 This method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

NOTE 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-μm), or No. 200 (75-μm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

NOTE 2—Two types of dispersion devices are provided: (*1*) a high-speed mechanical stirrer, and (*2*) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-μm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μm.

2. Referenced Documents

2.1 *ASTM Standards:*

D 421 Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

NOTE 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft³/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

NOTE 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 21, 1963. Originally published 1935. Replaces D 422 – 62.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.

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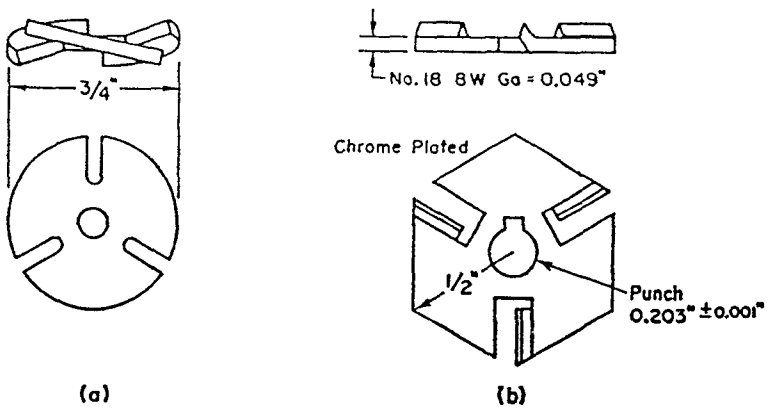


Metric Equivalents					
in.	0.001	0.049	0.203	½	¾
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles

3-in. (75-mm)	No. 10 (2.00-mm)
2-in. (50-mm)	No. 20 (850-μm)
1½-in. (37.5-mm)	No. 40 (425-μm)
1-in. (25.0-mm)	No. 60 (250-μm)
¾-in. (19.0-mm)	No. 140 (106-μm)
⅜-in. (9.5-mm)	No. 200 (75-μm)
No. 4 (4.75-mm)	

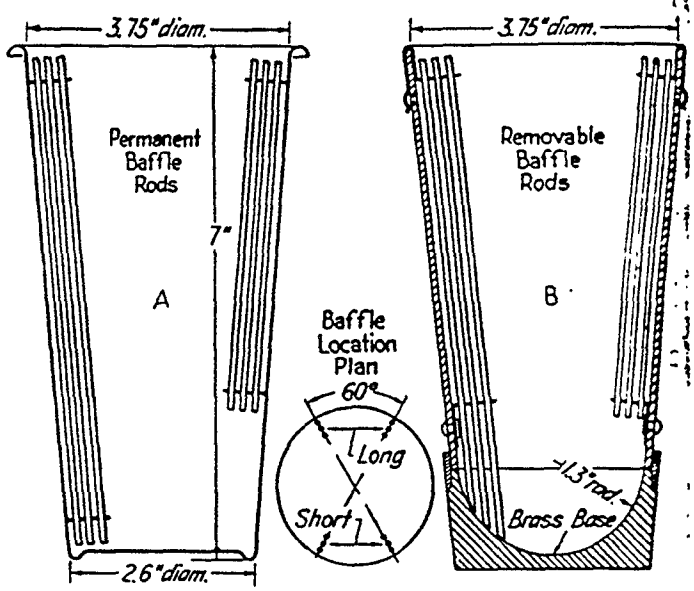
NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)	No. 16 (1.18-mm)
1½-in. (37.5-mm)	No. 30 (600-μm)
¾-in. (19.0-mm)	No. 50 (300-μm)
⅜-in. (9.5-mm)	No. 100 (150-μm)
No. 4 (4.75-mm)	No. 200 (75-μm)
No. 8 (2.36-mm)	

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-mL capacity.

3.9 *Timing Device*—A watch or clock with a second hand.



Metric Equivalents			
in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

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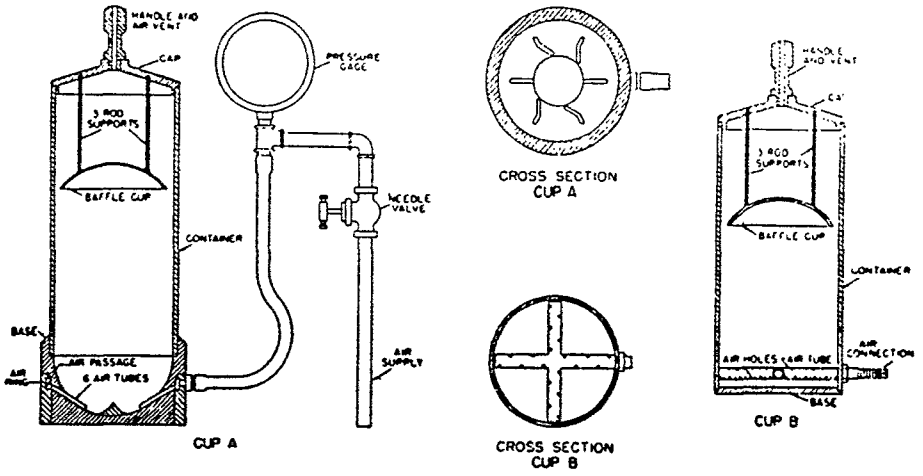


FIG. 3 Air-Jet Dispersion Cups of Apparatus B

5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Practice D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Practice D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
⅜ (9.5)	500
¾ (19.0)	1000
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

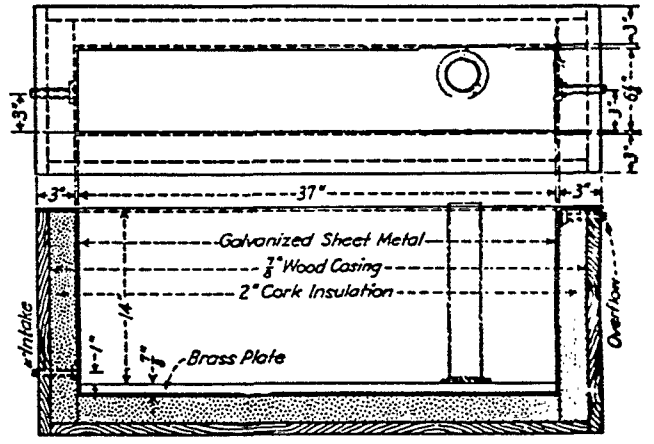
5.2 Provision is made in Section 5 of Practice D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.



Metric Equivalents

in.	⅞	1	3	6¼	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

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HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-mm) SIEVE

7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cyclinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hydrometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

9.5 Place the cover cap on the cup and open the air control valve until the gage pressure is 20 psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil - water slurry to the sedimentation cylinder.

10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns.

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Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-μm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

CALCULATIONS AND REPORT

12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

14. Percentages of Soil in Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

TABLE 1 Values of Correction Factor, a, for Different Specific Gravities of Soil Particles[A]

Specific Gravity	Correction Factor[A]
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W) \times 100$$

where:

a = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),

P = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,

R = hydrometer reading with composite correction applied (Section 7),

W = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,

G = specific gravity of the soil particles, and

G_1 = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G_1.

15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. According to Stokes' law:

$$D = \sqrt{[30n/980(G - G_1)]} \times L/t$$

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where:

D = diameter of particle, mm,

n = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

L = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

T = interval of time from beginning of sedimentation to the taking of the reading, min,

G = specific gravity of soil particles, and

G_1 = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows:

$$D = K\sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

15.3 Values of D may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of L is divided by T using the A- and B-scales, the square root being indicated on the D-scale. Without ascertaining the value of the square root it may be multiplied by K, using either the C- or CI-scale.

16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2), and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm	Actual Hydrometer Reading	Effective Depth, L, cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.6
1.005	15.0	5	15.5		
1.006	14.7	6	15.3	36	10.4
1.007	14.4	7	15.2	37	10.2
1.008	14.2	8	15.0	38	10.1
1.009	13.9	9	14.8	39	9.9
1.010	13.7	10	14.7	40	9.7
1.011	13.4	11	14.5	41	9.6
1.012	13.1	12	14.3	42	9.4
1.013	12.9	13	14.2	43	9.2
1.014	12.6	14	14.0	44	9.1
1.015	12.3	15	13.8	45	8.9
1.016	12.1	16	13.7	46	8.8
1.017	11.8	17	13.5	47	8.6
1.018	11.5	18	13.3	48	8.4
1.019	11.3	19	13.2	49	8.3
1.020	11.0	20	13.0	50	8.1
1.021	10.7	21	12.9	51	7.9
1.022	10.5	22	12.7	52	7.8
1.023	10.2	23	12.5	53	7.6
1.024	10.0	24	12.4	54	7.4
1.025	9.7	25	12.2	55	7.3
1.026	9.4	26	12.0	56	7.1
1.027	9.2	27	11.9	57	7.0
1.028	8.9	28	11.7	58	6.8
1.029	8.6	29	11.5	59	6.6
1.030	8.4	30	11.4	60	6.5
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

[A] Values of effective depth are calculated from the equation:

$$L = L_1 + \tfrac{1}{2}\,[L_2 - (V_B/A)]$$

where:

L = effective depth, cm,

L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,

L_2 = overall length of the hydrometer bulb, cm,

V_B = volume of hydrometer bulb, cm^3, and

A = cross-sectional area of sedimentation cylinder, cm^2

Values used in calculating the values in Table 2 are as follows:

For both hydrometers, 151H and 152H:

L_2 = 14.0 cm

V_B = 67.0 cm^3

A = 27.8 cm^2

For hydrometer 151H

L_1 = 10.5 cm for a reading of 1.000

= 2.3 cm for a reading of 1.031

For hydrometer 152H,

L_1 = 10.5 cm for a reading of 0 g/litre

= 2.3 cm for a reading of 50 g/litre

17. Graph

17.1 When the hydrometer analysis is performed, a graph

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TABLE 3 Values of K for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

Temperature, °C	Specific Gravity of Soil Particles							
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149

of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.

NOTE 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(1) Gravel, passing 3-in. and retained on No. 4 sieve ..... %
(2) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %
  (a) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %
  (b) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %
  (c) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %
(3) Silt size, 0.074 to 0.005 mm ..... %
(4) Clay size, smaller than 0.005 mm ..... %
  Colloids, smaller than 0.001 mm ..... %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS

Sieve Size	Percentage Passing
3-in.	.....
2-in.	.....
1½-in.	.....
1-in.	.....
¾-in.	.....
⅜-in.	.....
No. 4 (4.75-mm)	.....
No. 10 (2.00-mm)	.....
No. 40 (425-μm)	.....
No. 200 (75-μm)	

HYDROMETER ANALYSIS

0.074 mm
0.005 mm
0.001 mm

NOTE 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

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METHOD 1310

EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD
AND STRUCTURAL INTEGRITY TEST

1.0 SCOPE AND APPLICATION

1.1 This method is employed to determine whether a waste exhibits the characteristic of Extraction Procedure Toxicity.

1.2 The procedure may also be used to simulate the leaching which a waste will undergo if disposed of in a sanitary landfill. Method 1310 is applicable to liquid, solid, and multiphase samples.

2.0 SUMMARY OF METHOD

2.1 If a representative sample of the waste contains >0.5% solids, the solid phase of the sample is ground to pass a 9.5 mm sieve and extracted with deionized water which is maintained at a pH of 5 + 0.2, with acetic acid. Wastes that contain <0.5% solids are not subjected to extraction but are directly analyzed. Monolithic wastes which can be formed into a cylinder 3.3 cm (dia) x 7.1 cm, or from which such a cylinder can be formed which is representative of the waste, may be evaluated using the Structural Integrity Procedure instead of being ground to pass a 9.5-mm sieve.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Extractor: For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Examples of suitable extractors are shown in Figures 1-3 of this method and are available from: Associated Designs & Manufacturing Co., Alexandria, Virginia; Glas-Col Apparatus Co., Terre Haute, Indiana; Millipore, Bedford, Massachusetts; and Rexnard, Milwaukee, Wisconsin.

4.2 pH meter or pH controller: Accurate to 0.05 pH units with temperature compensation.

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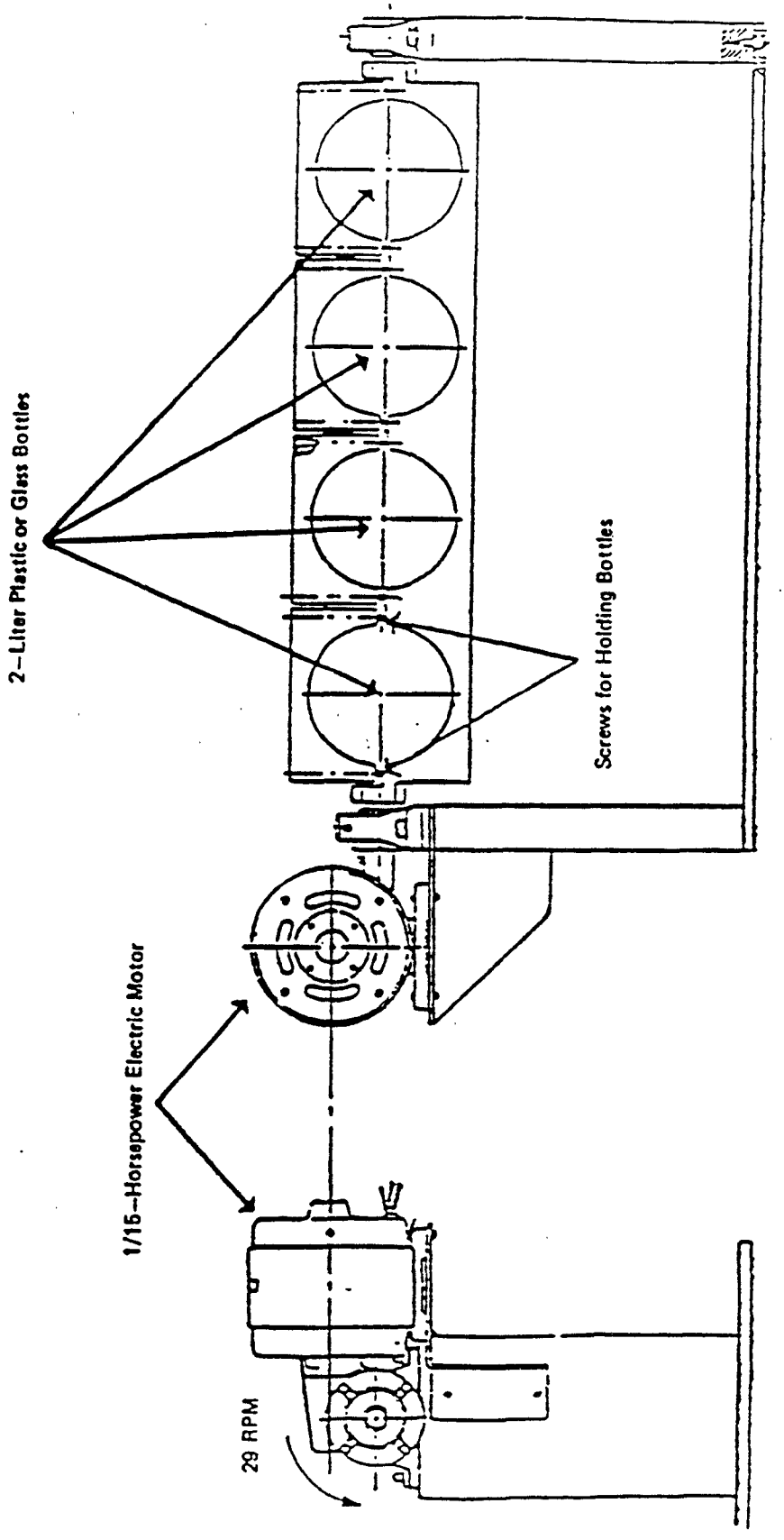


Figure 2. Rotary Extractor.

4.3 Filter holder: Capable of supporting a 0.45-um filter membrane and of withstanding the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex systems that can exert up to 5.3 kg/cm^3 (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to EPA and deemed suitable for use are listed in Table 1.

4.4 Filter membrane: Filter membrane suitable for conducting the required filtration shall be fabricated from a material that (1) is not physically changed by the waste material to be filtered and (2) does not absorb or leach the chemical species for which a waste's EP extract will be analyzed. Table 2 lists filter media known to the agency to be suitable for solid waste testing.

4.4.1 In cases of doubt about physical effects on the filter, contact the filter manufacturer to determine if the membrane or the prefilter is adversely affected by the particular waste. If no information is available, submerge the filter in the waste's liquid phase. A filter that undergoes visible physical change after 48 hr (i.e., curls, dissolves, shrinks, or swells) is unsuitable for use.

TABLE 1. EPA-APPROVED FILTER HOLDERS

Manufacturer	Size	Model No.	Comments
Vacuum Filters			
Nalgene	500 mL	44-0045	Disposable plastic unit, including prefilter, filter pads, and reservoir; can be used when solution is to be analyzed for inorganic constituents.
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
Pressure Filters			
Nuclepore	142 mm	425900	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

4.4.2 To test for absorbtion or leaching by the filter:

4.4.2.1 Prepare a standard solution of the chemical species of interest.

4.4.2.2 Analyze the standard for its concentration of the chemical species.

4.4.2.3 Filter the standard and reanalyze. If the concentration of the filtrate differs from that of the original standard, then the filter membrane leaches or absorbs one or more of the chemical species and is not usable in this test method.

4.5 Structural integrity tester: A device meeting the specifications shown in Figure 4 and having a 3.18-cm (1.25-in.)-diameter hammer weighing 0.33 kg (0.73 lb) with a free fall of 15.24 cm (6 in.) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet these specifications.

5.0 REAGENTS

5.1 Acetic acid (0.5 N): This can be made by diluting concentrated glacial acetic acid (17.5 N) by adding 57 mL glacial acetic acid to 1,000 mL of water and diluting to 2 liters. The glacial acetic acid should be of high purity and monitored for impurities.

5.2 Analytical standards should be prepared according to the applicable analytical methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Preservatives must not be added to samples.

6.3 Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

7.0 PROCEDURE

7.1 If the waste does not contain any free liquid, go to Step 7.9. If the sample is liquid or multiphase, continue as follows. Weigh filter membrane and prefilter to ±0.01 g. Handle membrane and prefilters with blunt curved-tip forceps or vacuum tweezers, or by applying suction with a pipet.

7.2 Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45-um membrane on the support screen and add prefilters in ascending order of pore size. Do not prewet filter membrane.

7.3 Weigh out a representative subsample of the waste (100-g minimum).

7.4 Allow slurries to stand, to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.5 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops. This liquid will constitute part or all of the extract (refer to Step 7.16). The liquid should be refrigerated until time of analysis.

NOTE: Oil samples or samples containing oil are treated in exactly the same way as any other sample. The liquid portion of the sample is filtered and treated as part of the EP extract. If the liquid portion of the sample will not pass through the filter (usually the case with heavy oils or greases), it should be carried through the EP extraction as a solid.

7.6 Remove the solid phase and filter media and, while not allowing them to dry, weigh to $\pm$0.01 g. The wet weight of the residue is determined by calculating the weight difference between the weight of the filters (Step 7.1) and the weight of the solid phase and the filter media.

7.7 The waste will be handled differently from this point on, depending on whether it contains more or less than 0.5% solids. If the sample appears to have $<$0.5% solids, determine the percent solids exactly (see Note below) by the following procedure:

7.7.1 Dry the filter and residue at 80°C until two successive weighings yield the same value.

7.7.2 Calculate the percent solids, using the following equation:

$$\frac{\text{weight of filtered solid and filters - tared weight of filters}}{\text{initial weight of waste material}} \times 100 = \% \text{ solids}$$

NOTE: This procedure is used only to determine whether the solid must be extracted or whether it can be discarded unextracted. It is not used in calculating the amount of water or acid to use in the extraction step. Do not extract solid material that has been dried at 80°C. A new sample will have to be used for extraction if a percent solids determination is performed.

acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction, and, if the pH rises above 5.2, 0.5 N acetic acid should be added to bring the pH down to 5.0 ± 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 mL of acid per g of solid. The mixture should be agitated for 24 hr and maintained at 20-40°C (68-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller, manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123, or its equivalent, in conjunction with a metering pump and reservoir of 0.5 N acetic acid. If such a system is not available, the following manual procedure shall be employed.

7.13.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

7.13.2 The pH of the solution should be checked, and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 ± 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-min intervals, moving to the next longer interval if the pH does not have to be adjusted >0.5 pH units.

7.13.3 The adjustment procedure should be continued for at least 6 hr.

7.13.4 If, at the end of the 24-hr extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 mL per g of solids) has not been added, the pH should be adjusted to 5.0 ± 0.2 and the extraction continued for an additional 4 hr, during which the pH should be adjusted at 1-hr intervals.

7.14 At the end of the extraction period, Type II water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = mL Type II water to be added;

W = weight in g of solid charged to extractor; and

A = mL of 0.5 N acetic acid added during extraction.

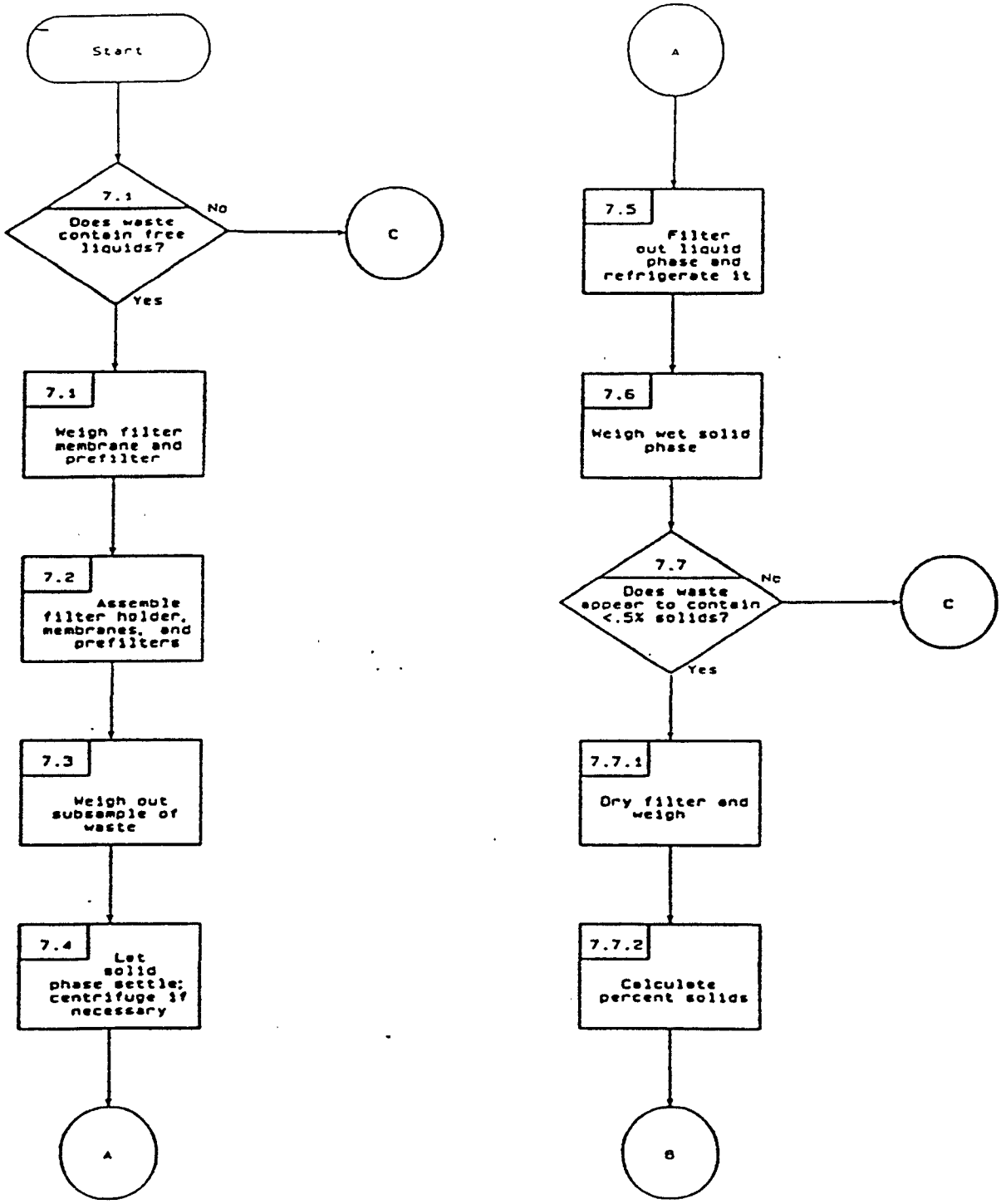
7.15 The material in the extractor should be separated into its component liquid and solid phases in the following manner:

7.15.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus (refer to Steps 4.3 and 4.4).

TABLE 3. PRECISIONS OF EXTRACTION-ANALYSIS PROCEDURES FOR SEVERAL ELEMENTS

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Arsenic	1. Auto fluff	7060	1.8, 1.5 ug/L
	2. Barrel sludge	7060	0.9, 2.6 ug/L
	3. Lumber treatment company sediment	7060	28, 42 mg/L
Barium	1. Lead smelting emission control dust	6010	0.12, 0.12 mg/L
	2. Auto fluff	7081	791, 780 ug/L
	3. Barrel sludge	7081	422, 380 ug/L
Cadmium	1. Lead smelting emission control dust	3010/7130	120, 120 mg/L
	2. Wastewater treatment sludge from electroplating	3010/7130	360, 290 mg/L
	3. Auto fluff	7131	470, 610 ug/L
	4. Barrel sludge	7131	1100, 890 ug/L
	5. Oil refinery tertiary pond sludge	7131	3.2, 1.9 ug/L
Chromium	1. Wastewater treatment sludge from electroplating	3010/7190	1.1, 1.2 mg/L
	2. Paint primer	7191	61, 43 ug/L
	3. Paint primer filter	7191	--
	4. Lumber treatment company sediment	7191	0.81, 0.89 mg/L
	5. Oil refinery tertiary pond sludge	7191	--
Mercury	1. Barrel sludge	7470	0.15, 0.09 ug/L
	2. Wastewater treatment sludge from electroplating	7470	1.4, 0.4 ug/L
	3. Lead smelting emission control dust	7470	0.4, 0.4 ug/L
Lead	1. Lead smelting emission control dust	3010/7420	940, 920 mg/L
	2. Auto fluff	7421	1540, 1490 ug/L
	3. Incinerator ash	7421	1000, 974 ug/L
	4. Barrel sludge	7421	2550, 2800 ug/L
	5. Oil refinery tertiary pond sludge	7421	31, 29 ug/L

(Continued)


Start
7.1
Does waste contain free liquids?
No
C
Yes
7.1
Weigh filter membrane and prefilter
7.2
Assemble filter holder, membranes, and prefilters
7.3
Weigh out subsample of waste
7.4
Let solid phase settle; centrifuge if necessary
A
A
7.5
Filter out liquid phase and refrigerate it
7.6
Weigh wet solid phase
7.7
Does waste appear to contain <.5% solids?
No
C
Yes
7.7.1
Dry filter and weigh
7.7.2
Calculate percent solids
B

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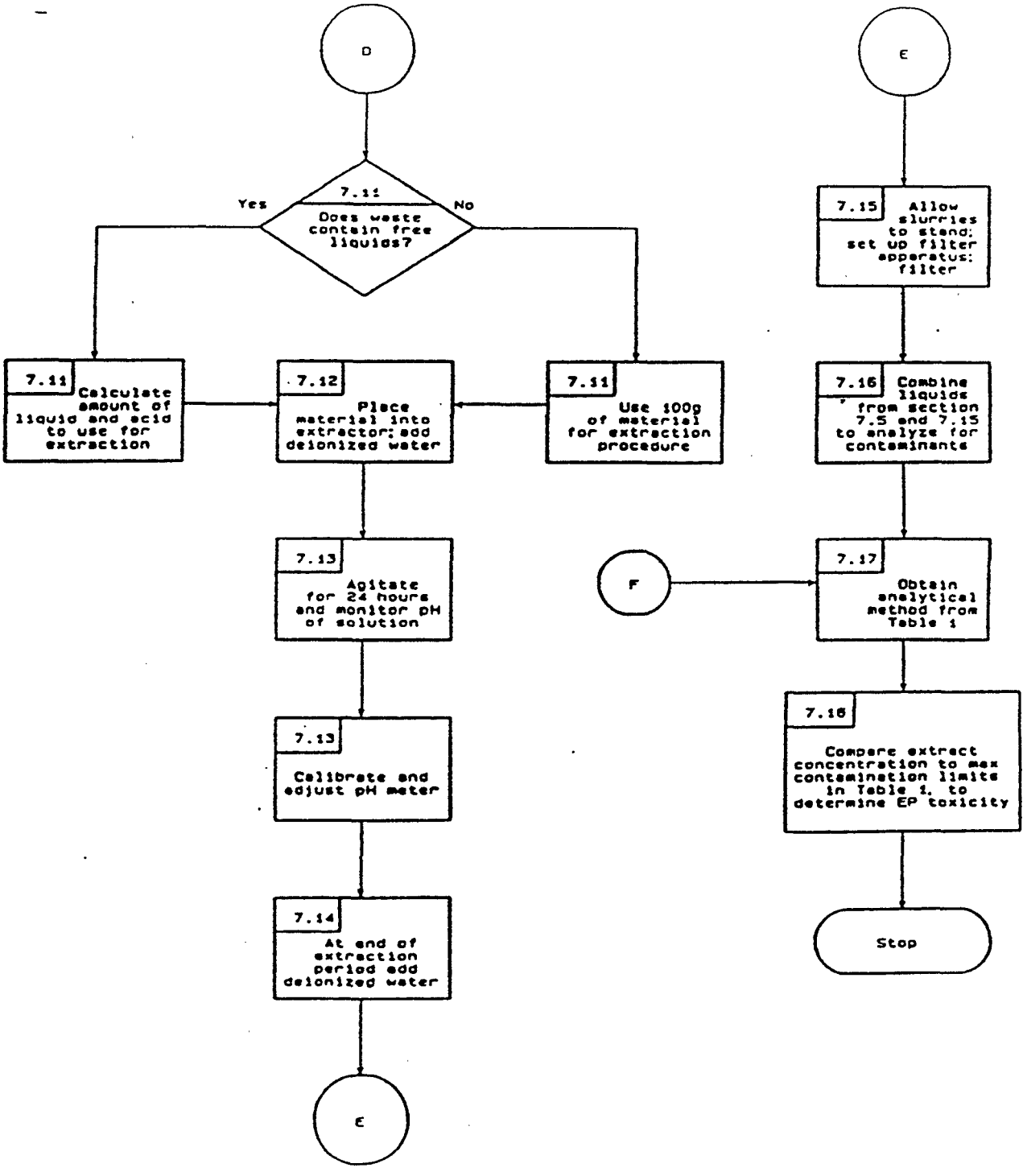
D
7.11
Does waste contain free liquids?
Yes
No
7.11
Calculate amount of liquid and acid to use for extraction
7.12
Place material into extractor; add deionized water
7.11
Use 100g of material for extraction procedure
7.13
Agitate for 24 hours and monitor pH of solution
7.13
Calibrate and adjust pH meter
7.14
At end of extraction period add deionized water
E
E
7.15
Allow slurries to stand; set up filter apparatus; filter
7.16
Combine liquids from section 7.5 and 7.15 to analyze for contaminants
F
7.17
Obtain analytical method from Table 1
7.18
Compare extract concentration to max contamination limits in Table 1, to determine EP toxicity
Stop

300543

Designation: D 1556 – 82[ε1]

Standard Test Method for Density of Soil in Place by the Sand-Cone Method[1]

This standard is issued under the fixed designation D 1556; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

[ε1] NOTE—Section 7.5.3 was changed editorially in December 1983.

1. Scope

1.1 This method covers the determination of the in-place density of soils.

1.2 Any soil or other material that can be excavated with hand tools can be tested provided the void or pore openings in the mass are small enough to prevent the sand used in the test from entering the natural voids. The soil or other material being tested should have sufficient cohesion or particle attraction to maintain stable sides on a small hole or excavation. It should also be firm enough to withstand the minor pressures exerted in digging the hole and placing the apparatus over it without deforming or sloughing.

1.3 When the moisture content and dry density are to be determined, this method is not to be used in certain soils or materials as indicated in paragraphs 1.3 and 3.5 of Method D2216.

2. Referenced Documents

2.1 *ASTM Standards:*

C136 Method for Sieve Analysis of Fine and Coarse Aggregates[2]

D653 Terminology Relating to Soil, Rock, and Contained Fluids[3]

D698 Test Methods for Moisture-Density Relations of Soils and Soil-Aggregate Mixtures Using 5.5-lb (2.49-kg) Rammer and 12-in. (305-mm) Drop[3]

D1557 Test Methods for Moisture-Density Relations of Soils and Soil-Aggregate Mixtures Using 10-lb (4.54-kg) Rammer and 18-in. (457-mm) Drop[3]

D2049 Test Method for Relative Density of Cohesionless Soils[4]

D2216 Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures[3]

3. Significance and Use

3.1 This method is used widely to determine the density of compacted soils used in the construction of earth embankments, road fill, and structure backfill. It is often used as the basis of acceptance for soils compacted to a specified density or percentage of a maximum density determined by a standard test method.

3.2 This method can be used to determine in-place density of natural soil deposits, aggregates, soil mixtures, or other similar material.

3.3 The use of this method is generally limited to soil in an unsaturated condition. This method is not recommended for soils that are soft or friable (crumble easily) or in a moisture condition such that water seeps into the hand-excavated hole. The accuracy of the test may be affected for soils that deform easily or that may undergo a volume change in the excavated hole from standing or walking near the hole during the test.

4. Apparatus

4.1 *Density Apparatus*, consisting of the following:

4.1.1 A jar or other container having a volume of approximately 1 gal (4000 cm³) or larger.

4.1.2 A detachable appliance consisting of a cylindrical valve with an orifice approximately ½ in. (13 mm) in diameter, having a small metal funnel connecting to a standard gal Mason jar top on one end and a large metal funnel (cone) on the other end. The valve shall have stops to prevent rotating it past the completely open or completely closed positions.

4.1.3 A square or rectangular metal plate with a flanged center hole cast or machined to receive the large funnel (cone) of the appliance described in 4.1.2. The plate shall be flat on the bottom and have sufficient thickness or stiffness to be rigid and shall have sidewalls approximately ⅜ to ½ in. (10 to 13 mm) high.

4.1.4 The details for the apparatus described herein are shown in Fig. 1 and represent the minimum acceptable dimensions suitable for testing soils having maximum particle sizes of approximately 2 in. (50 mm) and test hole volumes of approximately 0.1 ft³ (3000 cm³). When the material being tested contains a small amount of oversize and isolated large particles are encountered, the test can be moved to a new location. Larger apparatus and test hole volumes are needed when particles larger than 2 in. (50 mm) are prevalent.

NOTE 1—The apparatus described here represents a design that has proved satisfactory. Larger apparatus of similar proportions may be used as long as the basic principles of the sand volume determination are observed.

4.2 *Sand*, shall be clean, dry, uniform, uncemented, du-

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[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.08 on Special and Construction Control Tests.

Current edition approved Nov. 26, 1982. Published January 1983. Originally published as D 1556 – 58 T. Last previous edition D 1556 – 64 (1974).

[2] *Annual Book of ASTM Standards*, Vol 04.02.

[3] *Annual Book of ASTM Standards*, Vol 04.08.

[4] Discontinued, see *1983 Annual Book of ASTM Standards*, Vol 04.08.

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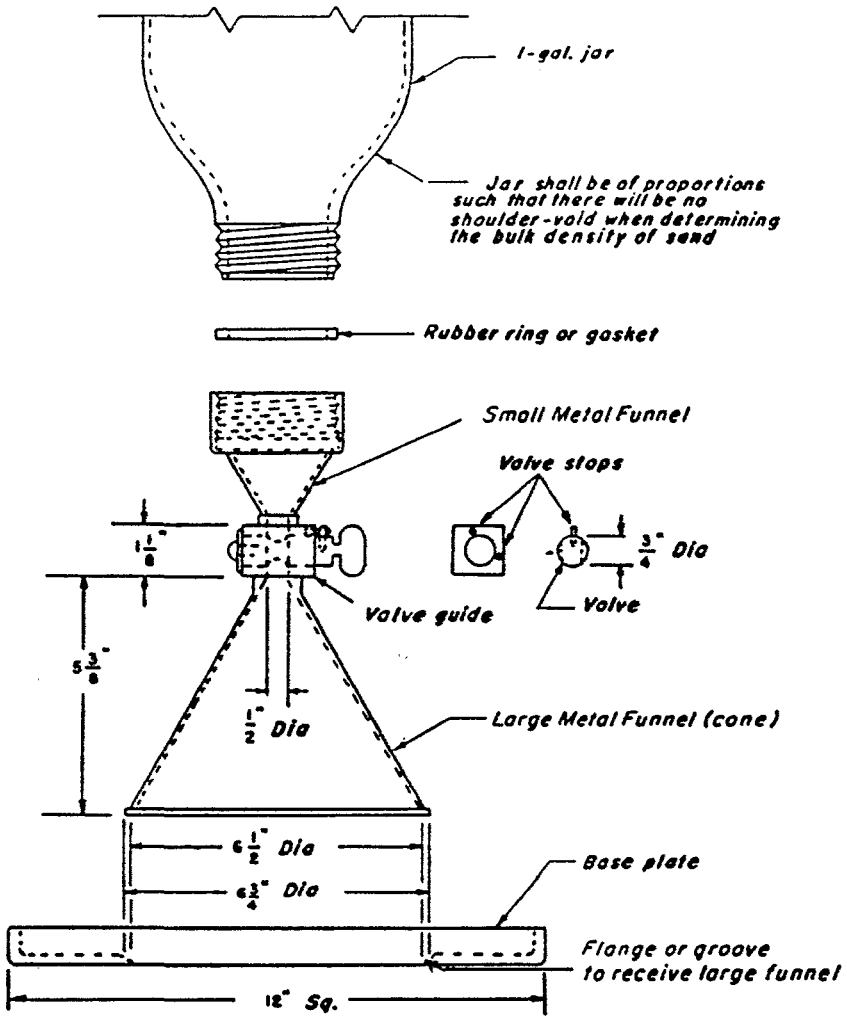

Metric Equivalents

in.	mm	in.	mm
1/2	12.7	5 3/8	136.5
3/4	19.1	6 1/2	165.1
1 1/8	28.6	6 3/4	171.5
		12	304.8

FIG. 1 Density Apparatus

rable, and free-flowing. Any gradation may be used that has a uniformity coefficient ($C_u = D_{60}/D_{10}$) less than 2.0, a maximum particle size less than 2.00 mm (No. 10 sieve), and less than 3 % by weight passing 250 µm (No. 60 sieve). The particle size distribution (gradation) shall be determined in accordance with Method C136. Uniform sand is needed to prevent segregation during handling, storage, and use. Sand free of fines and fine sand particles is needed to prevent significant bulk density changes with normal daily changes in atmospheric humidity. Sand comprised of durable, natural subrounded or rounded particles is desirable. Crushed sand or sand having angular particles may not be free flowing, a condition that can cause bridging resulting in inaccurate density determinations (Note 2). In selecting a sand from a potential source, five separate bulk-density determinations shall be made on each container or bag of sand. To be an acceptable sand, the variation between any determination and the average shall not be greater than 1% of the average. Before using sand in density determinations, it shall be dried, then allowed to reach an air-dried state in the general location where it is to be used. Sand shall not be reused without removing any contaminating soil, checking the gradation, and drying. Bulk-density tests shall be made at intervals not exceeding 14 days, always after any significant changes in atmospheric humidity, before reusing, and before using a new batch from a previously approved supplier (Note 3).

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NOTE 2—Some manufactured (crushed) sands such as blasting sand have been successfully used with good reproducibility. The reproducibility of test results using angular sand should be checked under actual testing situations before selecting an angular sand for use.

NOTE 3—Most sands have a tendency to absorb moisture from the atmosphere. A very small amount of absorbed moisture can make a substantial change in bulk density. In areas of high humidity or where the humidity changes often, the bulk density may need to be determined more often than the 14-day maximum interval indicated. The need for more frequent checks can be determined by comparing the results of different bulk-density tests on the same sand made in the area and conditions of use over a period of time.

4.3 *Balances*—A balance or scale of 10-kg capacity readable to 1.0 g and accurate to 2 g from 100 g to 7000 g and 3 g above 7000 g, and a balance of 2000 g capacity readable to 0.1 g and accurate to 0.1 %.

4.4 *Drying Equipment*—Oven, as specified in Method D2216 (See 6.1.10 and Note 6.)

4.5 *Miscellaneous Equipment*—Knife, small pick, chisel, small trowel, screwdriver, or spoons for digging test hole; buckets with lids, seamless tin or aluminum cans with lids, plastic-lined cloth sacks, or other suitable containers for retaining the density sample, moisture sample, and density sand respectively; thermometer for determining the temperature of water; small, paint-type brush, slide rule or calculator, notebook, etc.

5. Calibration

5.1 Determinations of mass are to be made to the nearest 1 g except for those required for determining moisture content, which shall be made to the nearest 0.1 g.

5.2 Determine the mass of sand required to fill the funnel and base plate as follows:

5.2.1 Put sand in the apparatus and determine the mass of apparatus and sand.

5.2.2 Place the base plate on a clean, level, plane surface. Invert the apparatus and seat the large funnel into the flanged center hole in the base plate, and mark and identify the funnel and plate so that the same funnel and plate can always be matched and reseated in the same position.

5.2.3 Open the valve and keep open until the sand stops running, making sure the apparatus, base plate, or plane surface are not jarred or vibrated before the valve is closed.

5.2.4 Close the valve sharply, determine the mass of the apparatus with remaining sand and calculate the loss of sand. This loss represents the mass of sand required to fill the funnel and base plate.

5.2.5 Repeat the procedures in 5.2.1 to 5.2.4 at least three times. The mass of sand used in the calculations shall be the average of three determinations. The maximum variation between any one determination and the average shall not exceed 1 %.

5.3 Use either Method A or Method B to determine the sand bulk density.

5.4 *Method A*—Determine the bulk density of the sand to be used in the field test as follows:

5.4.1 Select a known-volume container that is approximately the same size and allows the sand to fall approximately the same distance as the hole excavated in making a field test. The 1/30-ft³ (944-cm³) and 1/13.333-ft³ (2124-cm³) molds specified in Test Methods D698 or the 0.1-ft³ (2830-cm³) mold specified in Test Method D2049 are recommended.

5.4.2 Make measurements of sufficient accuracy to determine the volume of the container to ±1.0 %. The measurement tolerances for the above recommended molds are given in Test Methods D698 and D2049.

5.4.3 Flow characteristics through different valve assemblies have been known to cause different bulk-density values. The funnel and valve apparatus used to determine the bulk density of the sand shall be the same as used for making field tests unless other assemblies are determined to provide the same results.

5.4.4 Fill the assembled apparatus with sand.

5.4.5 Determine the mass of the known-volume container when empty.

5.4.6 Support the apparatus over the known-volume container in an inverted position so that the sand falls approximately the same distance as in a field test, and fully open the valve.

5.4.7 Fill the container until it just overflows and close the valve. Carefully strike off excess sand to a smooth level surface at the top of the container. Care must be taken so that the container is not jarred or vibrated before striking off is completed.

5.4.8 Clean any sand from the outside of the container and determine the mass of the known-volume container when full. Determine the net mass of sand by subtracting the mass of the empty container.

NOTE 4—When the known-volume container has the same diameter as the flanged center hole in the metal plate, the procedures in 5.4.6 to 5.4.8 can be simplified by using the plate on top of the known-volume container. Striking off the excess sand is not required when the apparatus with sand is weighed before and after filling the container and the mass required to fill the cone and plate (5.2.5) is subtracted from the difference.

5.4.9 Repeat the procedure in 5.4.4 to 5.4.8 at least three times. The mass used in the calculations shall be the average of three determinations. The maximum variation between any one determination and the average shall not exceed 1 %.

5.5 *Method B*—The bulk density of sand to be used in the field test is determined by first determining the volume of the jar and attachment up to and including the volume of the valve orifice then by using the jar to measure a volume and mass of sand as follows:

5.5.1 In making bulk density determinations, use a glass or other rigid jar that is well-rounded where it tapers toward the opening. Other jars may be used for making in-place density tests.

5.5.2 Use the same funnel and valve assembly for determining the bulk density of sand as will be used in field tests or determine that other assemblies provide the same results.

5.5.3 Use heavy grease or other waterproof substances in those stopcocks and thread assemblies that are not watertight.

5.5.4 Determine the mass of the assembled apparatus and record.

5.5.5 Place the apparatus upright and open the valve.

5.5.6 Fill the apparatus with water until it appears over the valve.

5.5.7 Close valve and remove excess water.

5.5.8 Determine the mass of the apparatus and water, and determine the temperature of the water to the nearest 1°C.

5.5.9 To determine the mass of the water to fill the apparatus, subtract the mass of the apparatus from the mass of the apparatus and the water.

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5.5.10 Repeat the procedure described in 5.5.4 to 5.5.9 at least three times. Convert the weight of water, in grams, to millilitres by correcting for the temperature as given in 7.3.1. The volume used shall be the average of three determinations with a maximum variation of 3 mL.

5.5.11 The volume determined in this procedure is constant as long as the jar and attachment are in the same relative position as the previous volume determination. If the two are to be separated, match marks should be made to permit reassembly to this position.

5.5.12 Completely dry the jar and other apparatus and remove any grease or waterproofing substances before proceeding with the following bulk density determination.

5.5.13 Place the empty apparatus upright on a firm level surface, close the valve, and fill the funnel with sand.

5.5.14 Open the valve and, keeping the funnel at least half full of sand, fill the apparatus, making sure the apparatus is not jarred or vibrated before the valve is closed. When the sand stops flowing, close the valve sharply and empty excess sand.

5.5.15 Determine the mass of the apparatus with sand and determine the net mass of sand by subtracting the mass of the apparatus.

5.5.16 Repeat the procedures in 5.5.13 to 5.5.15 at least three times. The mass used in the calculations shall be the average of three determinations. The maximum variation between any one determination and the average shall not exceed 1 %.

6. Procedure

6.1 Determine the density of the soil in place as follows:

6.1.1 Fill the apparatus with sand previously calibrated for bulk density and determine the mass of the apparatus and sand.

6.1.2 Prepare the surface of the location to be tested so that it is a level plane. The base plate makes an excellent tool for striking off the surface to a neat level plane.

6.1.3 Seat the base plate on the plane surface, making sure there is good contact with the ground surface around the edge of the flanged center hole. Mark the outline of the base plate to check for movement during the test, and use nails pushed into the soil adjacent to the edge of the plate or otherwise secure the plate against movement without disturbing the soil to be tested.

6.1.4 In soils where leveling is not successful, a preliminary test shall be run at this point measuring the volume bounded by the funnel plate and ground surface. Fill the space with sand from the apparatus, determine the mass of sand used to fill the space, refill the apparatus, and determine a new initial mass of apparatus and sand before proceeding with the test. After this measurement is completed, carefully brush the sand from the prepared surface.

NOTE 5—A second calibrated apparatus may be taken to the field when this condition is anticipated (instead of refilling and making a second mass determination). The procedure in 6.1.4 may be used for each test when the best possible accuracy is desired, however, it is usually not needed for most production testing where a relatively smooth surface is obtainable.

6.1.5 Dig the test hole inside the center hole in the base plate, being very careful to avoid disturbing the soil that will bound the hole. Test-hole volumes shall be as large as practical to minimize the effects of errors and shall in no case be smaller than the volume indicated in Table 1. The sides of the hole should slope inward slightly toward the bottom that should be reasonably flat or concave. The hole should be kept as free as possible of pockets, overhangs, and sharp obtrusions since these affect the accuracy of the test. Soils that are essentially granular require extreme care and may require digging a conical-shaped test hole. Place all excavated soil and soil loosened during excavation in a container that is marked to identify the test number. Take care to avoid losing any material. Protect this material from any loss of moisture until the mass has been determined and a specimen has been obtained for moisture content determination.

6.1.6 Clean the flange of the center hole in the metal plate, invert the apparatus, and seat the large metal funnel into the flanged hole at the same location as marked during calibration. Open the valve and allow the sand to fill the hole, funnel, and base plate. Take care to avoid jarring or vibrating the apparatus or the ground during this step. When the sand stops flowing, close the valve.

6.1.7 Determine the mass of the apparatus with remaining sand, and calculate the mass of sand used in the test.

6.1.8 Determine the mass of the material that was removed from the test hole.

6.1.9 Mix the material thoroughly and obtain a representative specimen for moisture-content determination or use the entire sample.

6.1.10 Determine the moisture content in accordance with Method D 2216.

NOTE 6—Rapid methods of moisture determination may be used to obtain an approximate value that is later verified or corrected according to the values obtained in accordance with Method D 2216.

6.2 Moisture-content specimens are to be large enough and selected in such a way so as to represent all the material

TABLE 1 Minimum Test Hole Volumes and Minimum Moisture Content Samples Based on Maximum Size of Particle

Maximum Particle Size	Minimum Test Hole Volume, cm^3	Minimum Test Hole Volume, ft^3	Minimum Moisture Content Sample, g
No. 4 Sieve (4.75 mm)	710	0.025	100
½ in. (12.5 mm)	1420	0.050	300
1 in. (25 mm)	2120	0.075	500
2 in. (50 mm)	2830	0.100	1000

TABLE 2 Volume of Water per Gram Based on Temperature

Temperature		Volume of Water, mL/g
°C	°F	
12	53.6	1.00048
14	57.2	1.00073
16	60.8	1.00103
18	64.4	1.00138
20	68.0	1.00177
22	71.6	1.00221
24	75.2	1.00268
26	78.8	1.00320
28	82.4	1.00375
30	86.0	1.00435
32	89.6	1.00497

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obtained from the test hole. Suggested minimum mass of moisture specimens in relation to maximum particle size are shown in Table 1.

7. Calculations

7.1 Calculations as shown are for using units in grams and cubic centimetres or millilitres. Other units are permissible provided the appropriate conversion factors are used to maintain consistency of units throughout the calculations.

7.2 *Sand Calibration—Method A*:

7.2.1 Calculate the bulk density of the sand as follows:

$$\rho_1 = M_1/V_1$$

where:

ρ_1 = bulk density of the sand, g/cm³, or multiply by 62.43 for lb/ft³,
M_1 = mass of sand to fill the known volume container, 5.4.9, g, and
V_1 = volume of the known volume container, 5.4.2, cm³.

7.3 *Sand Calibration—Method B*:

7.3.1 Calculate the volume of the density apparatus as follows:

$$V_2 = GT$$

where:

V_2 = volume of the density apparatus, mL,
G = mass of water required to fill the apparatus, 5.5.9, and
T = water temperature-volume correction shown in column 3 of Table 2.

7.3.2 Calculate the bulk density of the sand as follows:

$$\rho_1 = M_2/V_2$$

where:

ρ_1 = bulk density of the sand, g/cm³, or multiply by 62.43 for lb/ft³,
M_2 = mass of sand required to fill the apparatus 5.5.16, g, and
V_2 = volume of apparatus, 5.5.10.

7.5 *Field Test*:

7.5.1 Calculate the volume of the test hole as follows:

$$V = (M_3 - M_4)/\rho_1$$

where:

V = volume of the test hole, cm³,
M_3 = mass of sand to fill the test hole, funnel, and base plate, 6.1.7, g,
M_4 = mass of sand to fill the funnel and base plate, 5.2.5, g, and
ρ_1 = bulk density of the sand, 7.2.1 or 7.3.2, g/cm³.

7.5.2 Calculate the dry mass of material removed from the test hole as follows:

$$M_6 = 100\ M_5/(w + 100)$$

where:

w = percentage of moisture, in material from test hole, 6.1.10,
M_5 = moist mass of the material from the test hole, 6.1.8,
M_6 = dry mass of material from test hole, g, or multiply by 0.002205 for lb.

7.5.3 Calculate the in-place wet and dry density of the material tested as follows:

$$\rho_m = M_5/V$$
$$\rho_d = M_6/V$$

where:

V = volume of test hole, 7.5.1, cm³,
M_5 = moist mass of the material from the test hole, 6.1.8, g,
M_6 = dry mass of the material from the test hole, 7.5.2, g,
ρ_m = wet density of the tested material g/cm³ or multiply by 62.43 for lb/ft³, and
ρ_d = dry density of the tested material.

NOTE 7—It may be desired to express the in-place density as a percentage of some other density, for example, the laboratory maximum density determined in accordance with Method D 698. This relation can be determined by dividing the in-place density by the maximum density and multiplying by 100.

8. Precision and Accuracy

8.1 The precision and accuracy of this method has not been determined. No available methods provide absolute values of the density of soil in place against which this method can be compared. The variability of soil and the destructive nature of the test do not provide for repetitive duplication of test results to obtain a meaningful statistical evaluation. Accuracy is a function of the care exercised in performing the steps of the test giving particular attention to careful control to systematic repetition of procedures used.

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Designation: D 2216 – 80

An American National Standard

Standard Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures[1]

This standard is issued under the fixed designation D 2216; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the laboratory determination of the water (moisture) content of soil, rock, and soil-aggregate mixtures by weight. For simplicity, the word "material" hereinafter refers to either soil, rock, or soil-aggregate mixtures, whichever is most applicable.

1.2 The water content of a material is defined as the ratio, expressed as a percentage, of the mass of "pore" or "free" water in a given mass of material to the mass of the solid material particles.

1.3 This method does not give true representative results for: materials containing significant amounts of halloysite, montmorillonite, or gypsum minerals; highly organic soils; or, materials in which the pore water contains dissolved solids (such as salt in the case of marine deposits). For a material of the previously mentioned types, a modified method of testing or data calculation may be established to give results consistent with the purpose of the test.

2. Summary of Method

2.1 The practical application in determining the water content of a material is to determine the mass of water removed by drying the moist material (test specimen) to a constant mass in a drying oven controlled at 110 ± 5°C and to use this value as the mass of water in the test specimen. The mass of material remaining after oven-drying is used as the mass of the solid particles.

3. Significance and Use

3.1 For many soil types, the water content is one of the most significant index properties used in establishing a correlation between soil behavior and an index property.

3.2 The water content of a soil is used in almost every equation expressing the phase relationships of air, water, and solids in a given volume of material.

3.3 In fine-grained (cohesive) soils, the consistency of a given soil type depends on its water content. The water content of a soil, along with its liquid and plastic limit, is used to express its relative consistency or liquidity index.

3.4 The term "water" as used in geotechnical engineering is typically assumed to be "pore" or "free" water and not that which is hydrated to the mineral surfaces. Therefore, the water content of materials containing significant amounts of hydrated water at in-situ temperatures or less than 110°C can be misleading.

3.5 The term "solid particles" as used in geotechnical engineering, is typically assumed to mean naturally occurring mineral particles that are not readily soluble in water. Therefore, the water content of materials containing extraneous matter (such as cement, etc), water-soluble matter (such as salt) and highly organic matter typically require special treatment or a qualified definition of water content.

4. Apparatus

4.1 *Drying Oven*, thermostatically-controlled, preferably of the forced-draft type, and maintaining a uniform temperature of 110 ± 5°C throughout the drying chamber.

4.2 *Balances*, having a precision (repeatability) of ±0.01 g for specimens having a mass of 200 g or less, ±0.1 g for specimens having a mass of between 200 and 1000 g, or ±1 g for specimens having a mass greater than 1000 g.

4.3 *Specimen Containers*—Suitable containers made of material resistant to corrosion and a change in mass upon repeated heating, cooling, and cleaning. Containers with close-fitting lids shall be used for testing specimens having a mass of less than about 200 g; while for specimens having a mass greater than about 200 g, containers without lids may be used (Note 1). One container is needed for each water content determination.

NOTE 1—The purpose of close-fitting lids is to prevent loss of moisture from specimens before initial weighing and to prevent absorption of moisture from the atmosphere following drying and before final weighing.

4.4 *Desiccator*—A desiccator of suitable size (a convenient size is 200 to 250-mm diameter) containing a hydrous silica gel. This equipment is only recommended for use when containers having close-fitting lids are not used. See 7.4.1.

5. Samples

5.1 Keep the samples that are stored prior to testing in noncorrodible airtight containers at a temperature between approximately 3 and 30°C and in an area that prevents direct contact with sunlight.

5.2 The water content determination should be done as

[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.

Current edition approved May 30, 1980. Published July 1980. Originally published as D 2216 – 63 T. Last previous edition D 2216 – 71

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soon as practicable after sampling, especially if potentially corrodible containers (such as steel thin-walled tubes, paint cans, etc.) or sample bags are used.

6. Test Specimen

6.1 For water contents being determined in conjunction with another ASTM method, the method of specimen selection specified in that method controls.

6.2 The manner in which the test specimen is selected and its required mass is basically dependent on the purpose (application) of the test, type of material being tested, and the type of sample (specimen from another test, bag, tube, split-barrel, etc.). In all cases, however, a representative portion of the total sample shall be selected. If a layered soil or more than one soil type is encountered, select an average portion of individual portions or both, and note which portion(s) was tested in the report of the results.

6.2.1 For bulk samples, select the test specimen from the material after it has been thoroughly mixed. The mass of moist material selected shall be in accordance with the following table:

Sieve Retaining More Than About 10 % of Sample	Recommended Minimum Mass of Moist Specimen, g
2.0 mm (No. 10) sieve	100 to 200
4.75 mm (No. 4) sieve	300 to 500
19 mm	500 to 1000
38 mm	1500 to 3000
76 mm	5000 to 10 000

6.2.2 For small (jar) samples, select a representative portion in accordance with the following procedure:

6.2.2.1 For cohesionless soils, thoroughly mix the material, then select a test specimen having a mass of moist material in accordance with the table in 6.2.1. See Note 2.

6.2.2.2 For cohesive soils, remove about 3 mm of material from the exposed periphery of the sample and slice it in half (to check if the material is layered) prior to selecting the test specimen. If the soil is layered see 6.2. The mass of moist material selected should not be less than 25 g or should be in accordance with the table in 6.2.1 if coarse-grained particles are noted. (Note 2).

6.3 Using a test specimen smaller than the minimum mass indicated previously requires discretion, though it may be adequate for the purpose of the test. A specimen having a mass less than the previously indicated value shall be noted in the report of the results.

NOTE 2—In many cases, when working with a small sample containing a relatively large coarse-grained particle, it is appropriate not to include this particle in the test specimen. If this occurs, it should be noted in the report of the results.

7. Procedure

7.1 Select representative test specimens in accordance with Section 6.

7.2 Place the moist specimen in a clean, dry container of known mass (Note 3), set the lid securely in position, and determine the mass of the container and moist material using an appropriate balance (4.2). Record these values.

7.3 Remove the lid and place the container with moist material in a drying oven maintained at 110 ± 5°C and dry to a constant mass (Notes 4, 5, and 6).

NOTE 3—To assist in the oven-drying of large test specimens, they should be placed in containers having a large surface area (such as pans) and the material broken up into smaller aggregations.

NOTE 4—The time required to obtain constant mass will vary depending on the type of material, size of specimen, oven type and capacity, and other factors. The influence of these factors generally can be established by good judgment, and experience with the materials being tested and the apparatus being used. In most cases, drying a test specimen over night (about 16 h) is sufficient. In cases where there is doubt concerning the adequacy of drying, drying should be continued until the mass after two successive periods (greater than ½ h) of drying indicate an insignificant change (less than about 0.1 %). Specimens of sand may often be dried to constant mass in a period of about 4 h, when a forced-draft oven is used.

NOTE 5—Oven-drying at 110 ± 5°C does not always result in water content values related to the intended use or the basic definition especially for materials containing gypsum or other minerals having significant amounts of hydrated water or for soil containing a significant amount of organic material. In many cases, and depending on the intended use for these types of materials, it might be more applicable to maintain the drying oven at 60 ± 5°C or use a vacuum desiccator at a vacuum of approximately 133 Pa (10 mm Hg) and at a temperature ranging between 23 and 60°C for drying. If either of these drying methods are used, it should be noted in the report of the results.

NOTE 6—Since some dry materials may absorb moisture from moist specimens, dried specimens should be removed before placing moist specimens in the oven. However, this requirement is not applicable if the previously dried specimens will remain in the drying oven for an additional time period of about 16 h.

7.4 After the material has dried to constant mass remove the container from the oven and replace the lid. Allow the material and container to cool to room temperature or until the container can be handled comfortably with bare hands and the operation of the balance will not be affected by convection currents. Determine the mass of the container and oven-dried material using the same balance as used in 7.2. Record this value.

7.4.1 If the container does not have a lid, weigh the container and material right after their temperatures are such that the operation of the balance will not be affected by convection currents or after cooling in a desiccator.

NOTE 7—Cooling in a desiccator is recommended since it prevents absorption of moisture from the atmosphere during cooling.

8. Calculation

8.1 Calculate the water content of the material as follows:

$$w = [(W_1 - W_2)/(W_2 - W_c)] \times 100 = \frac{W_w}{W_s} \times 100$$

where:

w = water content, %,
W_1 = mass of container and moist specimen, g,
W_2 = mass of container and oven-dried specimen, g,
W_c = mass of container, g,
W_w = mass of water, g, and
W_s = mass of solid particles, g.

9. Report

9.1 The report (data sheet) shall include the following.

9.1.1 Identification of the sample (material) being tested, by boring number, sample number, test number, etc.

9.1.2 Water content of the specimen to the nearest 0.1 % or 1 %, depending on the purpose of the test.

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9.1.3 Indication of test specimen having a mass less than the minimum indicated in Section 6.

9.1.4 Indication of test specimen containing more than one soil type (layered, etc).

9.1.5 Indication of the method of drying if different from oven-drying at 110 ± 5°C.

9.1.6 Indication of any material (size and amount) e cluded from the test specimen.

10. Precision and Accuracy

10.1 Requirements for the precision and accuracy of tl test method have not yet been developed.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

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METHOD 3005

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface water and ground water samples for analysis by flame atomic absorption spectroscopy (FAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

*ICP only

1.2 For the analysis of total dissolved metals, the sample is filtered at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals: The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals: The sample is filtered through a 0.5 um filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is again filtered (if necessary) and diluted to volume and is then ready for analysis.

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3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes.

4.2 Watch glasses.

4.3 Qualitative filter paper and filter funnels.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine level of impurities. If method blank is <MDL, then acid can be used.

5.3 Concentrated hydrochloric acid, reagent grade (HCl): Acid should be analyzed to determine level of impurities. If method blank is <MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Sampling:

6.3.1 **Total recoverable metals:** All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 **Dissolved metals:** All samples must be filtered through a 0.5 um filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed by FLAA or ICP, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass and heated on a steam bath or hot plate at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with Type II water.

8.0 QUALITY CONTROL

8.1 For each analytical batch of samples processed, blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 No data provided.

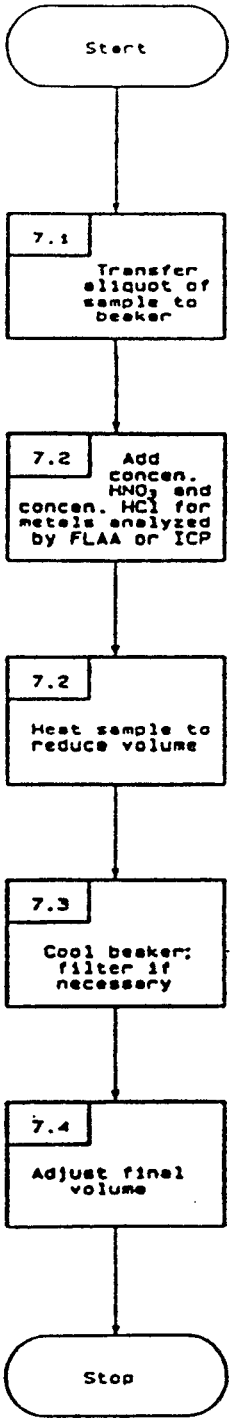
10.0 REFERENCES

10.1 None required.

METHOD 3005

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR

DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY



Revision 0
Date September 1986

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METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Paragraph 2.1):

FLAA		GFAA
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Potassium	Cobalt
Chromium	Sodium	Iron
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		Vanadium

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Mo, Pb, Ni, K, Na, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V. A separate sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

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4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers: 250-mL.
4.2 Watch glasses.
4.3 Drying ovens: That can be maintained at 30°C.
4.4 Thermometer: That covers range of 0 to 200°C.
4.5 Whatman No. 41 filter paper (or equivalent).
4.6 Centrifuge and centrifuge tubes.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid, reagent grade (HNO_3): Acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

5.3 Concentrated hydrochloric acid, reagent grade (HCl): Acid should be analyzed to determine level of impurities. If method blank is <MDL, the acid can be used.

5.4 Hydrogen peroxide (30%) (H_2O_2): Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqeuous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.00- to 2.00-g portion of sample.

7.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation.

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Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.
NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.5.2 **Centrifugation:** Centrifugation at 2,000-3,000 rpm for 10 min is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.6.2 **Centrifugation:** Centrifugation at 2,000-3,000 for 10 min is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

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7.7 Calculations:

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 For each group of samples processed, preparation blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

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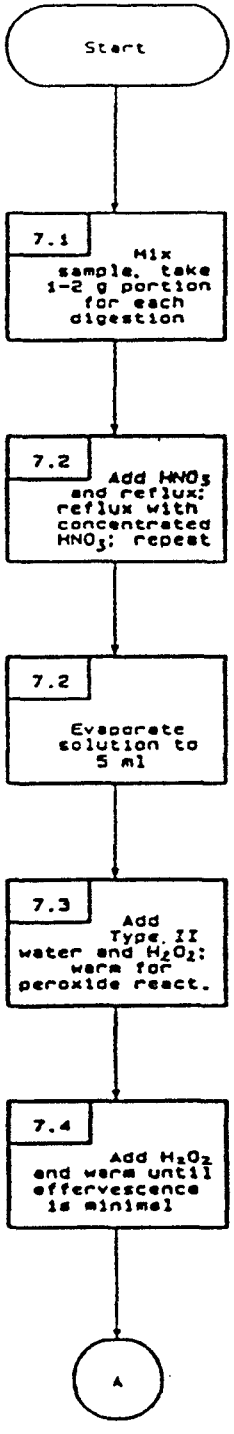
Start
7.1
Mix sample, take 1-2 g portion for each digestion
7.2
Add HNO_3 and reflux; reflux with concentrated HNO_3; repeat
7.2
Evaporate solution to 5 ml
7.3
Add Type II water and H_2O_2; warm for peroxide react.
7.4
Add H_2O_2 and warm until effervescence is minimal
A

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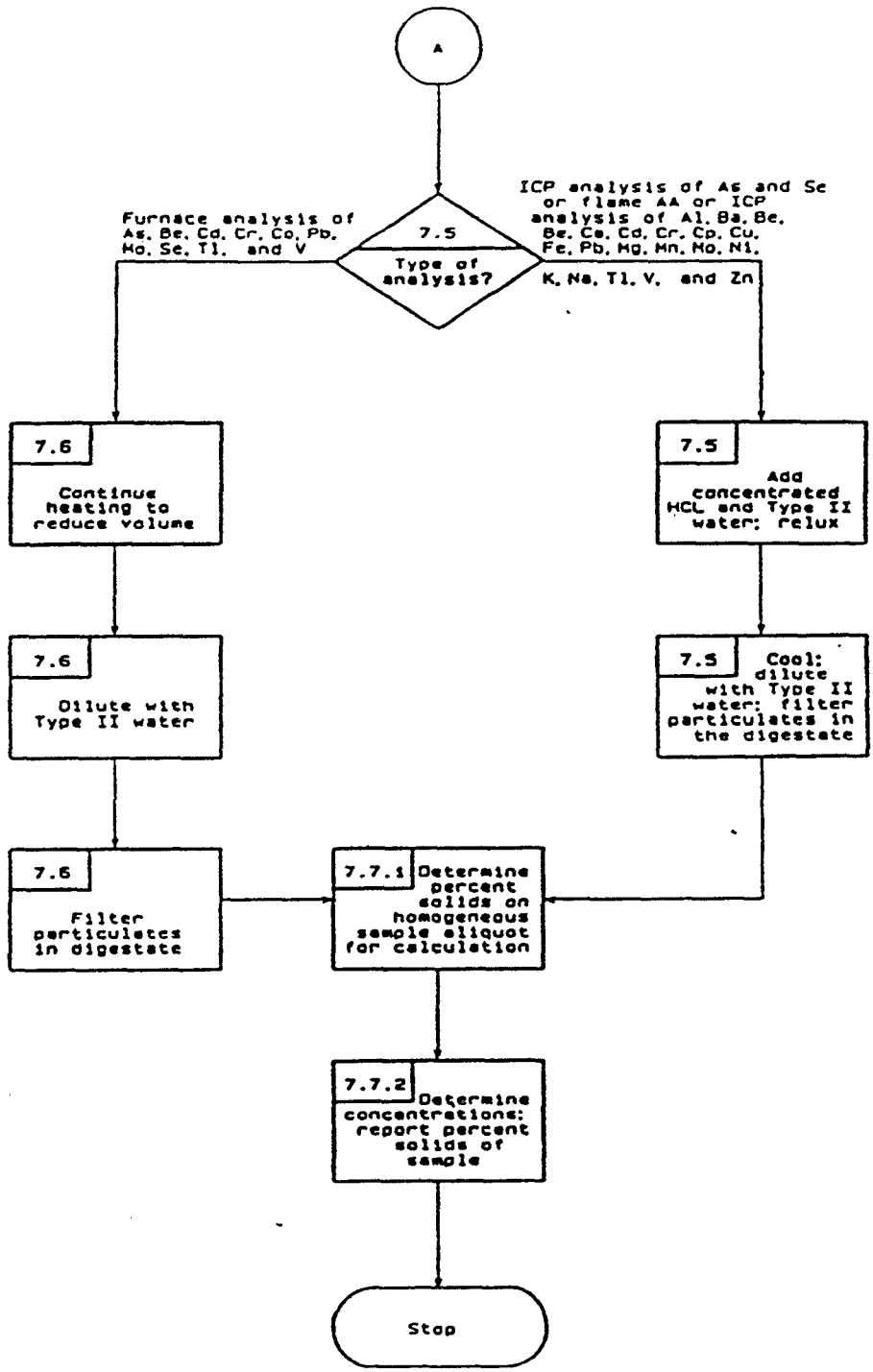
A
7.5
Type of analysis?
Furnace analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V
ICP analysis of As and Se or flame AA or ICP analysis of Al, Ba, Be, Be, Ca, Cd, Cr, Cp, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn
7.6
Continue heating to reduce volume
7.6
Dilute with Type II water
7.6
Filter particulates in digestate
7.5
Add concentrated HCL and Type II water; relux
7.5
Cool; dilute with Type II water; filter particulates in the digestate
7.7.1
Determine percent solids on homogeneous sample aliquot for calculation
7.7.2
Determine concentrations; report percent solids of sample
Stop

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METHOD 6010

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma atomic emission spectroscopy (ICP) determines elements including metals in solution. The method is applicable to a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

1.3 The method of standard addition (MSA) (Paragraph 8.5.3) shall be used for the analysis of all EP extracts and sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g., Methods 3005-3050).

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5.

TABLE 1. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Estimated Detection Limit[b] (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See note c
Selenium	196.026	75
Silicon	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Paragraph 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multielement instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 The interference is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a

TABLE 2. ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelength (nm)	Interferent [a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	—	—	—	—	—	—	0.21	—	—	1.4
Antimony	206.833	0.47	—	2.9	—	0.08	—	—	—	0.25	0.45
Arsenic	193.696	1.3	—	0.44	—	—	—	—	—	—	1.1
Barium	455.403	—	—	—	—	—	—	—	—	—	—
Beryllium	313.042	—	—	—	—	—	—	—	—	0.04	0.05
Boron	249.773	0.04	—	—	—	0.32	—	—	—	—	—
Cadmium	226.502	—	—	—	—	0.03	—	—	0.02	—	—
Calcium	317.933	—	—	0.08	—	0.01	0.01	0.04	—	0.03	0.03
Chromium	267.716	—	—	—	—	0.003	—	0.04	—	—	0.04
Cobalt	228.616	—	—	0.03	—	0.005	—	—	0.03	0.15	—
Copper	324.754	—	—	—	—	0.003	—	—	—	0.05	0.02
Iron	259.940	—	—	—	—	—	—	0.12	—	—	—
Lead	220.353	0.17	—	—	—	—	—	—	—	—	—
Magnesium	279.079	—	0.02	0.11	—	0.13	—	0.25	—	0.07	0.12
Manganese	257.610	0.005	—	0.01	—	0.002	0.002	—	—	—	—
Molybdenum	202.030	0.05	—	—	—	0.03	—	—	—	—	—
Nickel	231.604	—	—	—	—	—	—	—	—	—	—
Selenium	196.026	0.23	—	—	—	0.09	—	—	—	—	—
Silicon	288.158	—	—	0.07	—	—	—	—	—	—	0.01
Sodium	588.995	—	—	—	—	—	—	—	—	0.08	—
Thallium	190.864	0.30	—	—	—	—	—	—	—	—	—
Vanadium	292.402	—	—	0.05	—	0.005	—	—	—	0.02	—
Zinc	213.856	—	—	—	0.14	—	—	—	0.29	—	—

[a]Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L,
Ca - 1000 mg/L,
Cr - 200 mg/L,
Cu - 200 mg/L
Fe - 1000 mg/L
Mg - 1000 mg/L,
Mn - 200 mg/L,
Tl - 200 mg/L,
V - 200 mg/L

[b]The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

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tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio frequency generator.

4.1.3 Argon gas supply: Welding grade or better.

4.2 Operating conditions: The analyst should follow the instructions provided by the instrument's manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be reagent grade or better. Redistilled acids may be used.

5.1.1 Concentrated hydrochloric acid (HCl).

5.1.2 Hydrochloric acid (1:1): Add 500 mL concentrated HCl to 400 mL Type II water and dilute to 1 liter.

5.1.3 Concentrated nitric acid (HNO_3).

5.1.4 Nitric acid (1:1): Add 500 mL concentrated HNO_3 to 400 mL Type II water and dilute to 1 liter.

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5.2 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hr at 105°C, unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.)

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolve 0.10 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1:1) HCl and dilute to 1,000 mL with Type II water.

5.3.2 Antimony solution, stock, 1 mL = 100 ug Sb: Dissolve 0.27 g $K(SbO)C_4H_4O_6$ (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in Type II water, add 10 mL (1:1) HCl, and dilute to 1,000 mL with Type II water.

5.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.13 g of As_2O_3 (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of Type II water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.15 g $BaCl_2$ (mole fraction Ba = 0.6595), dried at 250°C for 2 hr, weighed accurately to at least four significant figures, in 10 mL Type II water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with Type II water.

5.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.97 g $BeSO_4 \cdot 4H_2O$ (mole fraction Be = 0.0509), weighed accurately to at least four significant figures, in Type II water, add 10.0 ml concentrated HNO_3, and dilute to 1,000 mL with Type II water. Mole fraction = 0.0509.

5.3.6 Boron solution, stock 1 mL = 100 ug B: Do not dry. Dissolve 0.57 g anhydrous H_3BO_3 (mole fraction B = 0.1748), weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered, and store in a desiccator to prevent the entrance of atmospheric moisture.

5.3.7 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.11 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.8 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.25 g $CaCO_3$ (mole Ca fraction = 0.4005), dried at 180°C for 1 hr before weighing, weighed accurately to at least four significant figures, in Type II water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.9 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.19 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in Type II water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.10 Cobalt solution, stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with Type II water.

5.3.11 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.13 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.12 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.14 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to 1,000 mL with Type II water.

5.3.13 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.16 g $Pb(NO_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to 1,000 mL with Type II water.

5.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.17 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to 1,000 mL with Type II water.

5.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.20 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL with Type II water.

5.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to 1,000 mL with Type II water.

5.3.18 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.19 g KCl (mole fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL.

5.3.19 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.17 g H_2SeO_3 (mole fraction Se = 0.6123), weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL.

5.3.20 Silica solution, stock, 1 mL = 100 ug SiO_2: Do not dry. Dissolve 0.47 g $Na_2SiO_3\cdot 9H_2O$ (mole fraction Si = 0.09884), weighed accurately to at least four significant figures, in Type II water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.21 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.16 g $AgNO_3$ (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in Type II water and 10 mL concentrated HNO_3. Dilute to 1,000 mL with Type II water.

5.3.22 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.25 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in Type II water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.23 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.13 g $TlNO_3$ (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in Type II water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.24 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.23 g NH_4VO_3 (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.25 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.12 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.4 Mixed calibration standard solutions: Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add 2 mL (1:1) HNO_3 and 10 mL of (1:1) HCl and dilute to 100 mL with Type II water (see NOTE, below). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Paragraph 5.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of Type II water and warm the flask until the solution clears. Cool and dilute to 100 mL with Type II water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni
V	Ag (see Note to Paragraph 5.4), B, Mg, Sb, and Tl

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5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by diluting 2 mL of (1:1) HNO_3 and 10 mL of (1:1) HCl to 100 mL with Type II water. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Paragraph 8.6.2.1 for use).

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of all matrices is always necessary because of the complexity and variability of sample matrices. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005-3050). The method of standard addition (MSA) (Paragraph 8.5.3) shall be used for the analysis of all EP extracts and sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required. An internal standard may be substituted for the MSA.

7.2 Set up the instrument with proper operating parameters established in Paragraph 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Paragraph 5.4. Flush the system with the calibration blank (5.5.1) between each standard (see NOTE, below). (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.)

NOTE: For boron concentrations greater than 500 ug/L, extended flush times of 1 or 2 min may be required.

7.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

7.5 Flush the system with the calibration blank solution for at least 1 min (Paragraph 5.5.1) before the analysis of each sample (see Note to Paragraph 7.3). Analyze the instrument check standard (5.6) and the calibration blank (5.5.1) after each 10 samples.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in ug/L with up to three significant figures.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one laboratory blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Analyze one duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 8.5.1 through 8.5.3, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Matrix spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis procedure can usually compensate for this effect.

CAUTION: The standard-addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.5.3 Standard addition: The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of Volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration c_S. To the second (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_X is calculated:

$$c_X = \frac{S_B V_S c_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and c_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus c_S is much greater than c_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the analyte added must respond the same way as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

8.6 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

8.6.1 Check instrument calibration using a calibration blank and two appropriate standards.

8.6.2 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (5.5.1) and a single point check standard (5.6).

8.6.2.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.2.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.3 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check sample (Paragraph 5.7). Results should be within ±20% of the true value obtained in 8.6.2.1.

8.6.4 Duplicate spiked samples are to be analyzed at a frequency of 20%.

8.6.4.1 The relative percent difference between duplicate determinations is to be calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

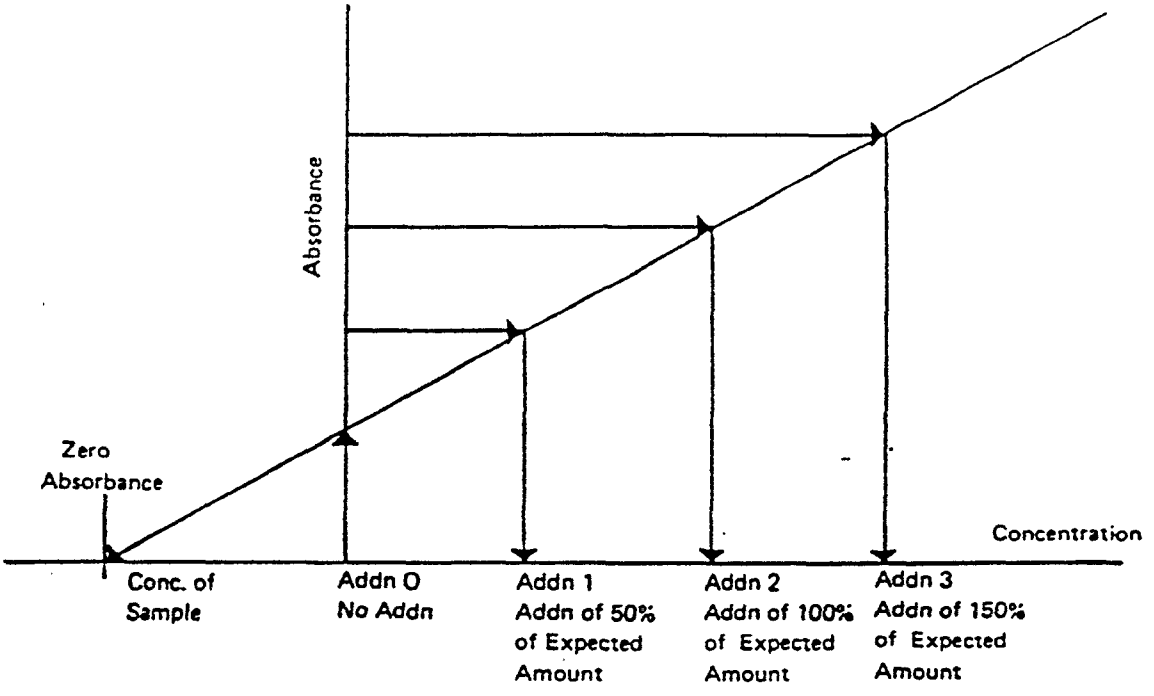

Figure 1. Standard Addition Plot.

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where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate).

(A control limit of ±20% for RPD shall be used for sample values greater than 10 times the instrument detection limit.)

8.6.4.2 The duplicate matrix spike sample recovery is to be within ±20% of the actual value.

8.6.5 The method of standard addition (Paragraph 8.5.3) shall be used for the analysis of all EP extracts.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9±2%. The mean percent recovery of spiked elements for all wastes was 93±6%. Spike levels ranged from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

10.0 REFERENCES

1. Winge, R.K., V.J. Peterson, and V.A. Fassel, Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines, Final Report, March 1977 - February 1978, Ames Laboratory, Ames, IA, sponsored by Environmental Research Laboratory, Athens, GA, EPA-600/4-79-017, March 1979.

2. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-05, December 1982, Method 200.7.

3. Patel, B.K., Raab, G.A., et al., Report on a Single Laboratory Evaluation of Inductively Coupled Optical Emission Method 6010, EPA Contract No. 68-03-3050, December 1984.

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se[c]	40	32	21.9	6	8.5	42	10	8.5	8.3

[a]Not all elements were analyzed by all laboratories.

[b]SD = standard deviation.

[c]Results for Se are from two laboratories.

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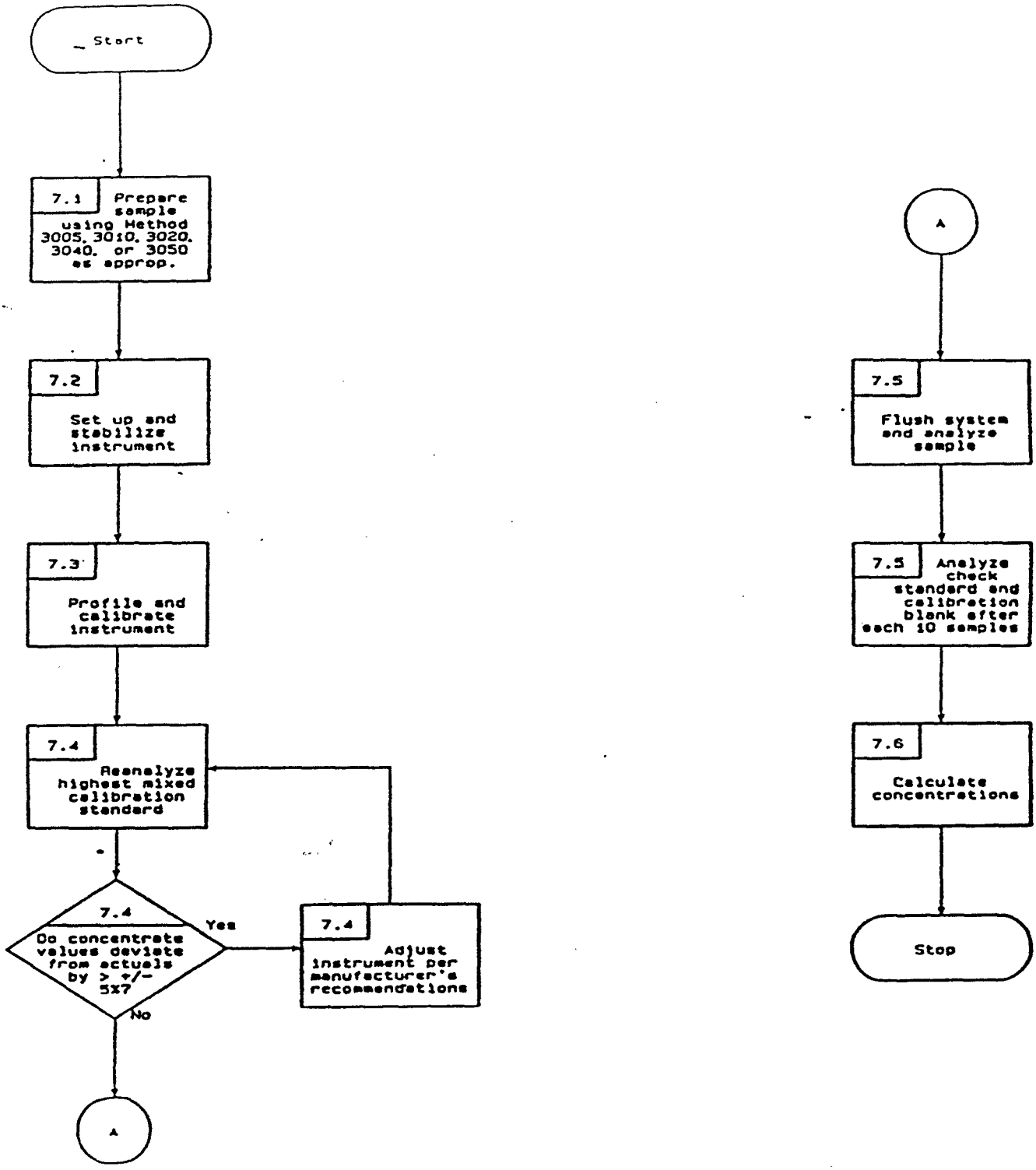
Start
7.1 Prepare sample using Method 3005, 3010, 3020, 3040, or 3050 as approp.
7.2 Set up and stabilize instrument
7.3 Profile and calibrate instrument
7.4 Reanalyze highest mixed calibration standard
7.4 Do concentrate values deviate from actuals by > +/- 5%?
Yes
No
7.4 Adjust instrument per manufacturer's recommendations
A
A
7.5 Flush system and analyze sample
7.5 Analyze check standard and calibration blank after each 10 samples
7.6 Calculate concentrations
Stop

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METHOD 7040

ANTIMONY (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In the presence of lead (1,000 mg/L), a spectral interference may occur at the 217.6-nm resonance line. In this case, the 231.1-nm antimony line should be used.

3.3 Increasing the acid concentrations decreases the antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

3.4 Excess concentrations of copper and nickel (and possibly other elements), as well as acids, can interfere with antimony analyses. If the sample contains these matrix types, either matrices of the standards should be matched to those of the sample or the sample should be analyzed using a nitrous oxide/acetylene flame.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Antimony hollow cathode lamp or electrodeless discharge lamp.
4.2.2 Wavelength: 217.6 nm (primary); 231.1 nm (secondary).
4.2.3 Fuel: Acetylene.
4.2.4 Oxidant: Air.
4.2.5 Type of flame: Fuel lean.
4.2.6 Background correction: Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

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5.2 Preparation of standards:

5.2.1 Stock solution: Carefully weigh 2.7426 g of antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ (analytical reagent grade), and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% v/v HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration Procedure.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-40 mg/L with a wavelength of 217.6 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.2 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 5.0 and 15 mg Sb/L gave the standard deviations of ± 0.08 and ± 0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

9.3 For concentrations of antimony below 0.35 mg/L, the furnace procedure (Method 7041) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.1.

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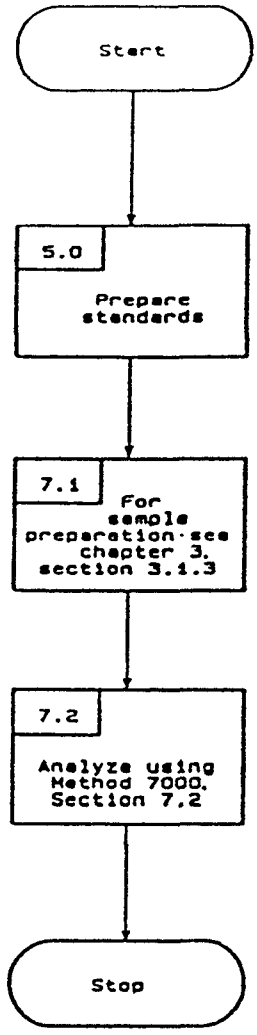
Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.1.3
7.2
Analyze using Method 7000, Section 7.2
Stop

300583

METHOD 7041

ANTIMONY (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High lead concentration may cause a measurable spectral interference on the 217.6-nm line. If this interference is expected, the secondary wavelength should be employed or Zeeman background correction used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.
4.2.2 Ashing time and temp: 30 sec at 800°C.
4.2.3 Atomizing time and temp: 10 sec at 2700°C.
4.2.4 Purge gas: Argon or nitrogen.
4.2.5 Wavelength: 217.6 nm (primary); 231.1 nm (alternate).
4.2.6 Background correction: Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

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5.2 Preparation of standards:

5.2.1 Stock solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% (v/v) HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

NOTE: The addition of HCl acid to the digestate prevents the furnace analysis of this digestate for many other metals.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

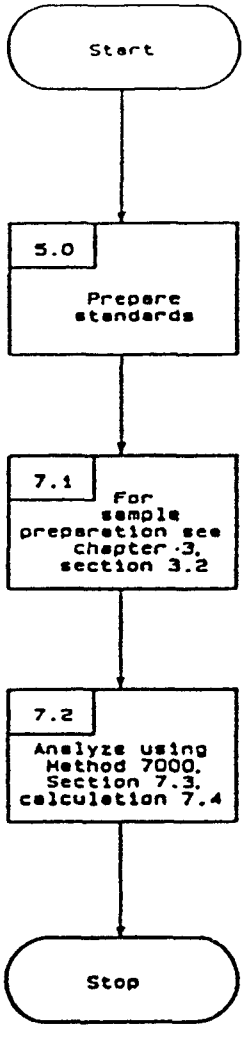
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 20-300 ug/L.
Detection limit: 3 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

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METHOD 7420

LEAD (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required at either wavelength.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Lead hollow cathode lamp.
4.2.2 Wavelength: 283.3 nm (primary); 217.0 nm (alternate).
4.2.3 Fuel: Acetylene.
4.2.4 Oxidant: Air.
4.2.5 Type of flame: Oxidizing (fuel lean).
4.2.6 Background correction: Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

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6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 283.3 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.1 mg/L.

9.2 For concentrations of lead below 0.2 mg/L, the furnace technique (Method 7421) is recommended.

9.3 Precision and accuracy data are available in Method 239.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

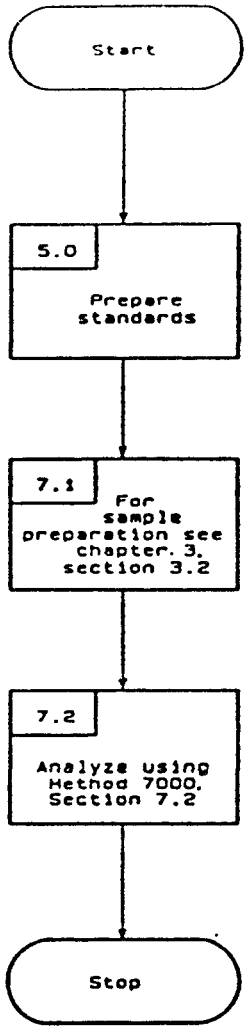
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 239.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	450, 404 ug/g
Emission control dust	3050	42,500, 63,600 ug/g


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7421

LEAD (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 If poor recoveries are obtained, a matrix modifier may be necessary. Add 10 uL of phosphoric acid (Paragraph 5.3) to 1 mL of prepared sample in the furnace sampler cup and mix well.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30°sec at 125°C.
4.2.2 Ashing time and temp: 30°sec at 500°C.
4.2.3 Atomizing time and temp: 10 sec at 2700°C.
4.2.4 Purge gas: Argon.
4.2.5 Wavelength: 283.3 nm.
4.2.6 Background correction: Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

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5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

5.3 Phosphoric acid: Reagent grade.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 239.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Lead by Flameless Atomic Absorption with Phosphate Matrix Modification, Atomic Spectroscopy, 1 (1980), no. 3, pp. 80-81.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

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TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	163, 120 mg/g
Paint primer	3050	0.55, 0.63 mg/g
Lagoon soil	3050	10.1, 10.0 ug/g
NBS SRM 1646 Estuarine sediment	3050	23.7 ug/g[a]
NBS SRM 1085 Wear metals in lubricating oil	3030	274, 298 ug/g[b]
Solvent extracted oily waste	3030	9, 18 ug/L

[a]Bias of -16% from expected.

[b]Bias of -10 and -2% from expected, respectively.

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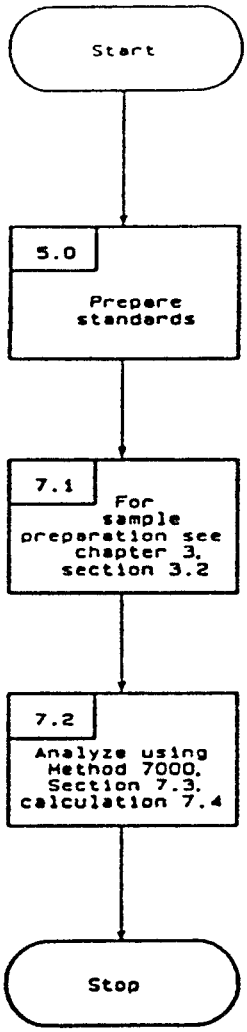
Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

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METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCBs

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a halogen-specific detector (HSD).

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

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TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs[a]

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method Detection limit (ug/L)
Aldrin	2.40	4.10	0.004
α-BHC	1.35	1.82	0.003
β-BHC	1.90	1.97	0.006
δ-BHC	2.15	2.20	0.009
γ-BHC (Lindane)	1.70	2.13	0.004
Chlordane (technical)	e	e	0.014
4,4'-DDD	7.83	9.08	0.011
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.003
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
Toxaphene	e	e	0.24
PCB-1016	e	e	nd
PCB-1221	e	e	nd
PCB-1232	e	e	nd
PCB-1242	e	e	0.065
PCB-1248	e	e	nd
PCB-1254	e	e	nd
PCB-1260	e	e	nd

[a]U.S. EPA. Method 617. Organochloride Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

300599

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns:

4.1.2.1 Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8-m x 4-mm I.D. glass column or equivalent.

4.1.2.2 Column 2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8-m x 4-mm I.D. glass column or equivalent.

4.1.3 Detectors: Electron capture (ECD) or halogen specific (HSD) (i.e., electrolytic conductivity detector).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.2.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, toluene, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference than GC/MS, a secondary surrogate is to be used when sample interference is apparent. Dibutylchlorendate (DBC) is also subject to acid and base degradation. Therefore, two surrogate standards are added to each sample; however, only one need be calculated for recovery. DBC is the primary surrogate and should be used whenever possible. However, if DBC recovery is low or compounds interfere with DBC, then the 2,4,5,6-tetrachloro-meta-xylene should be evaluated for acceptance. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500, Section 5.3.2, indicates the proper procedure for preparing these surrogates.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature is set at 200°C isothermal. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature held isothermal at 200°C. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow so that 4,4'-DDT has a retention time of approximately 12 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-level standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for various pesticides and PCBs are shown in Figures 1 through 5.

7.4.4 Prime the column as per Paragraph 7.3.2.

7.4.5 DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-level standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in Section 7.7 of Method 8000. Calculate percent breakdown as follows:

$$\% \text{ breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

7.4.6 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.7 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove Sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10-mL hexane extracts obtained from Paragraph 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.6 Calculations (exerpted from U.S. FDA, PAM):

7.6.1 **Calculation of Certain Residues:** Residues which are mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. In the following sections suggestions are offered for handling toxaphene, chlordane, PCB, DDT, and BHC. A column 10% DC-200 stationary phase was used to obtain the chromatograms in Figures 6-9.

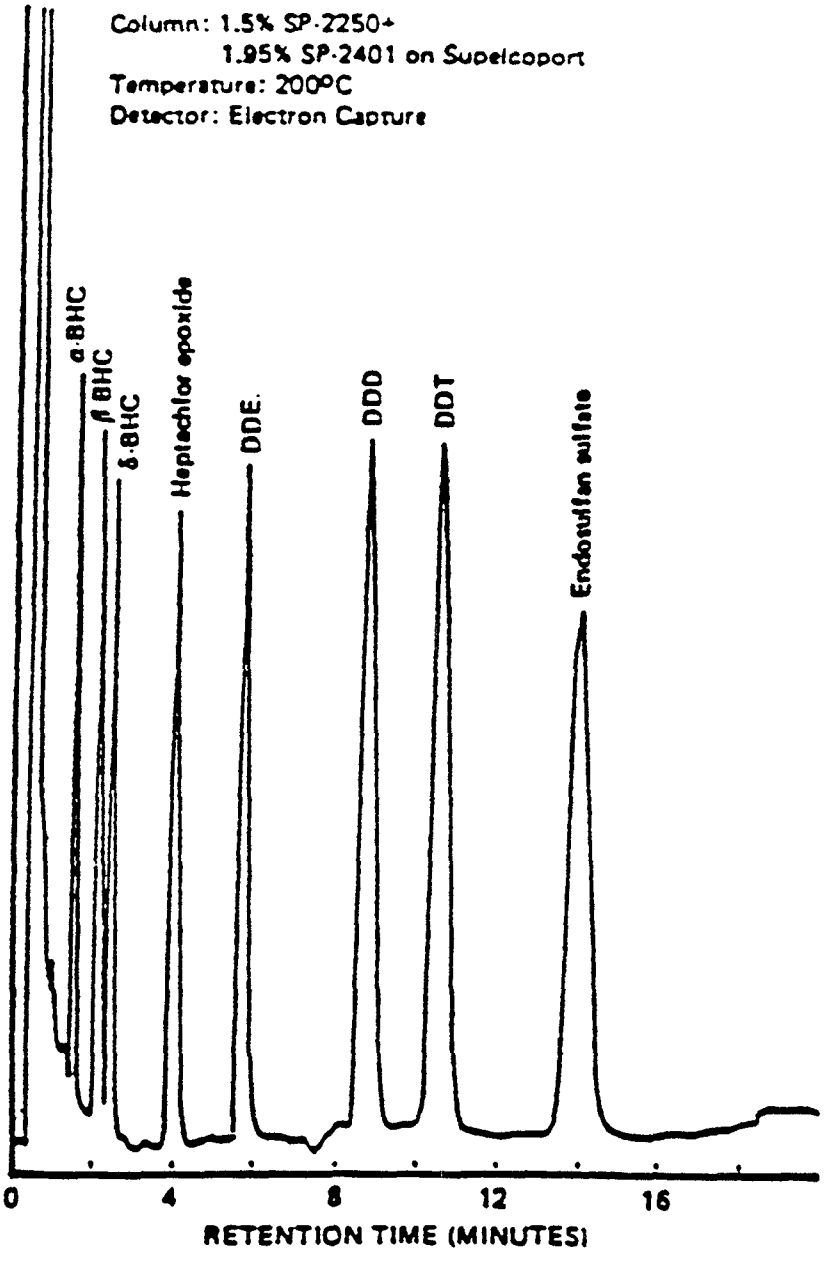

Figure 1. Gas chromatogram of pesticides.

300605

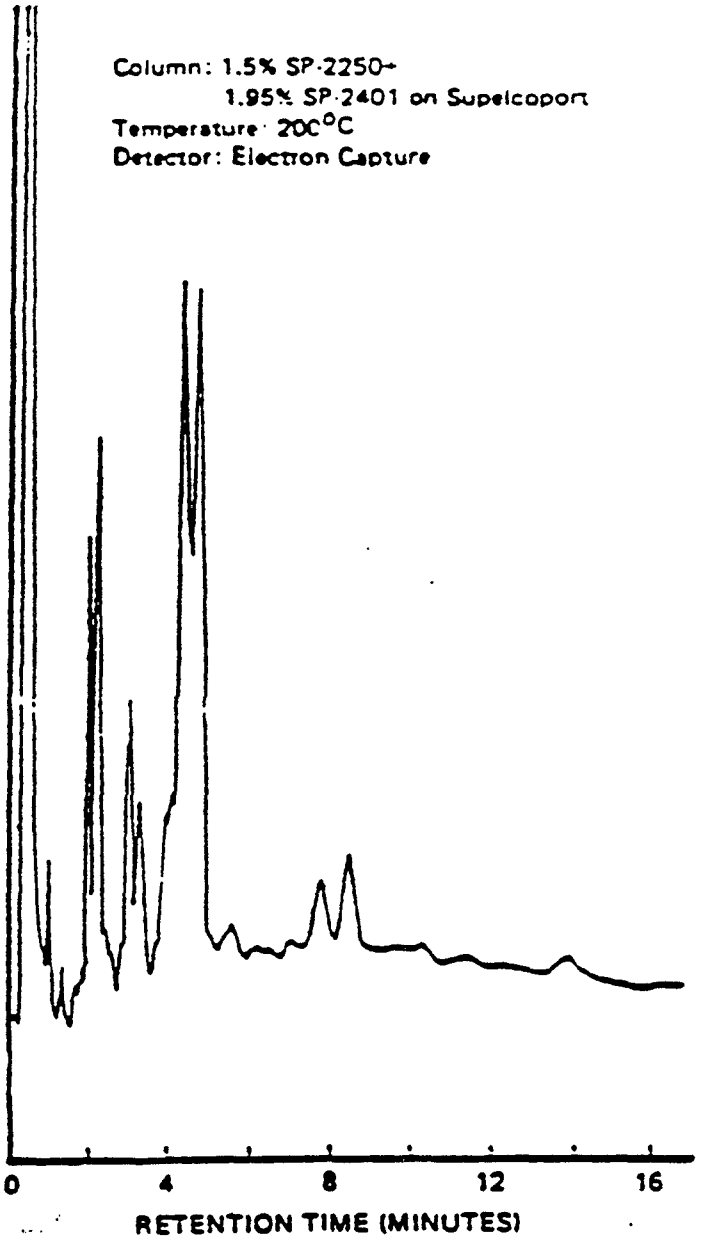

Figure 2. Gas chromatogram of chlordane.

300606

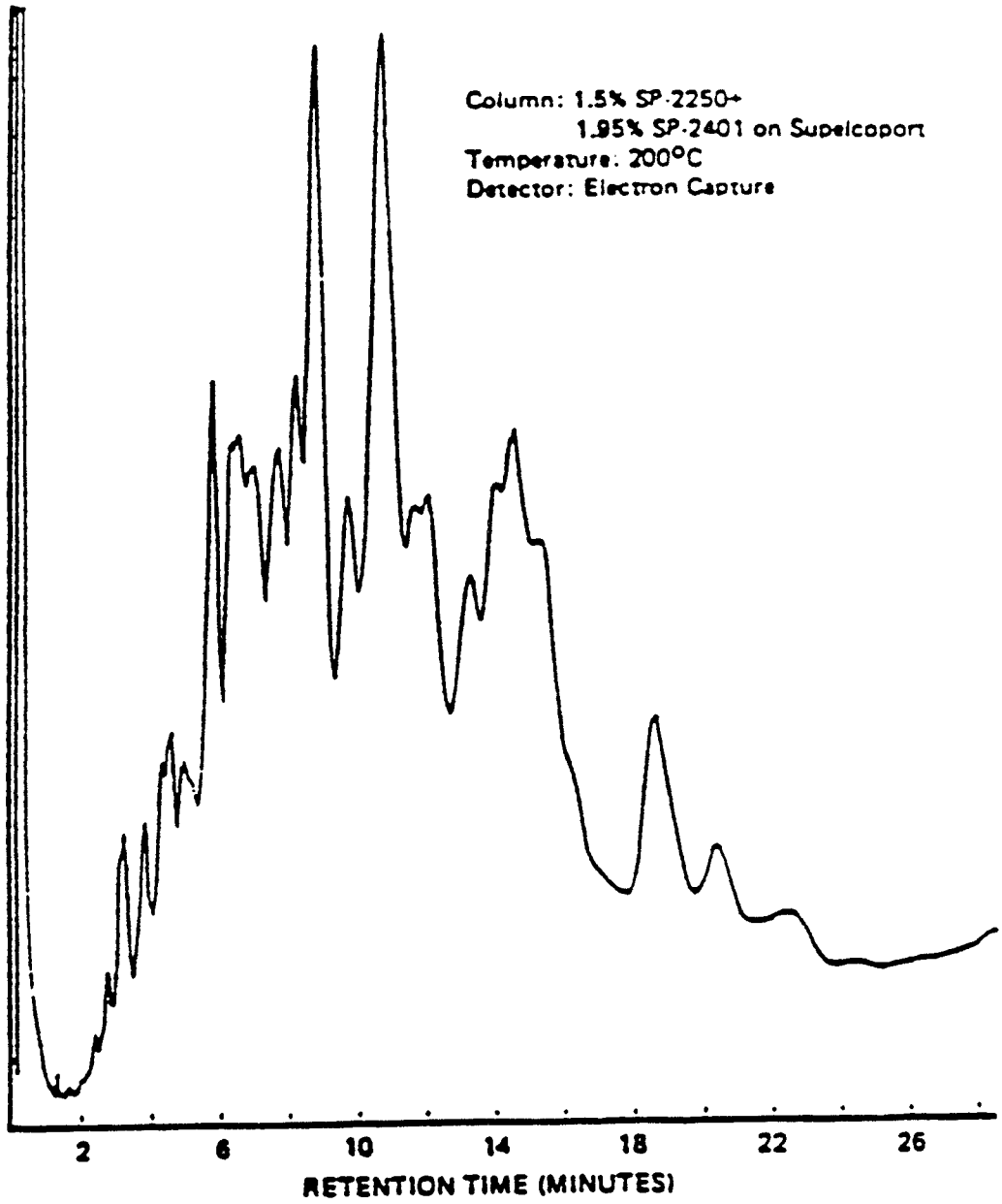

Figure 3. Gas chromatogram of toxaphene.

300607

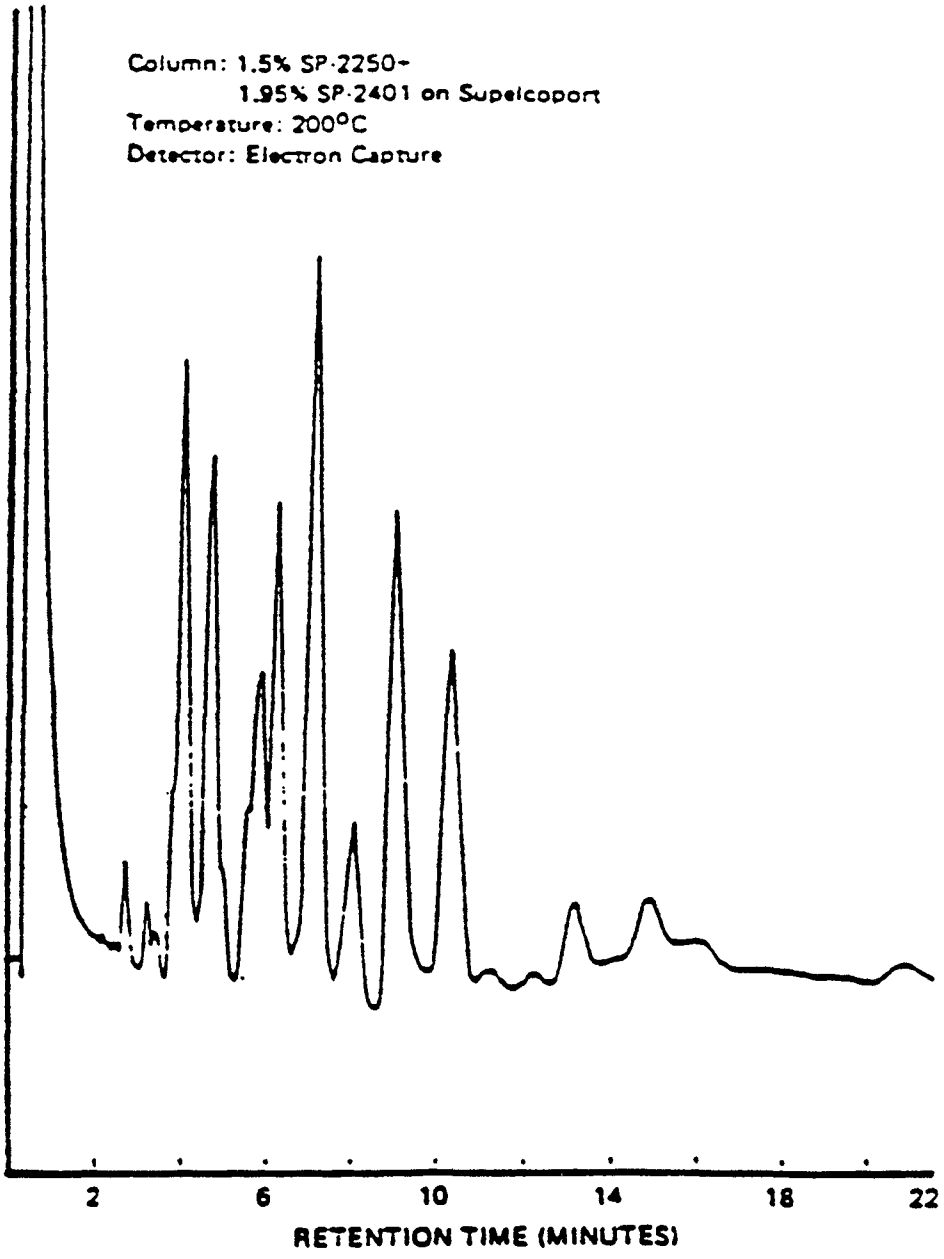

Figure 4. Gas chromatogram of PCB-1254.

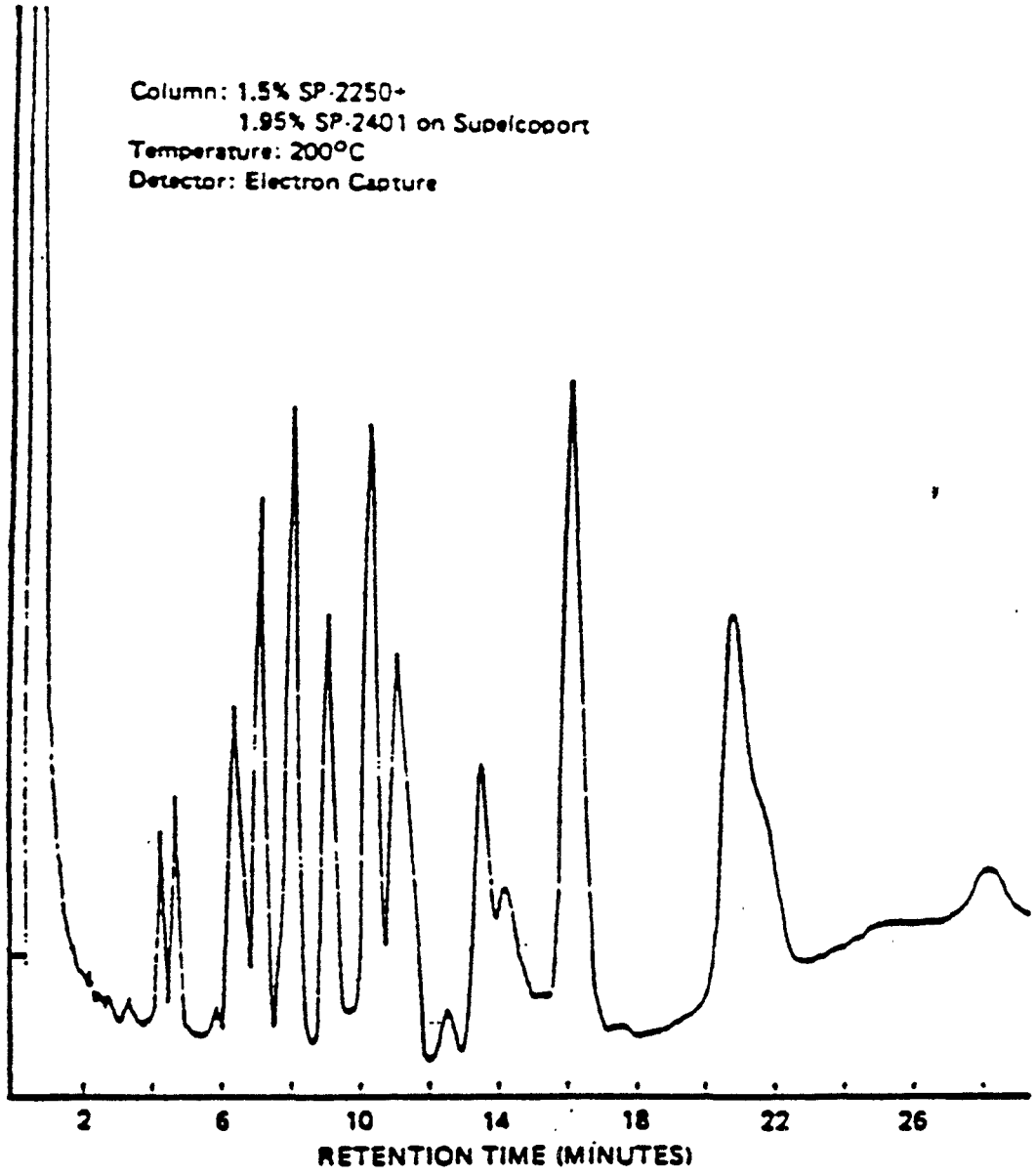

Figure 5. Gas chromatogram of PCB-1260.

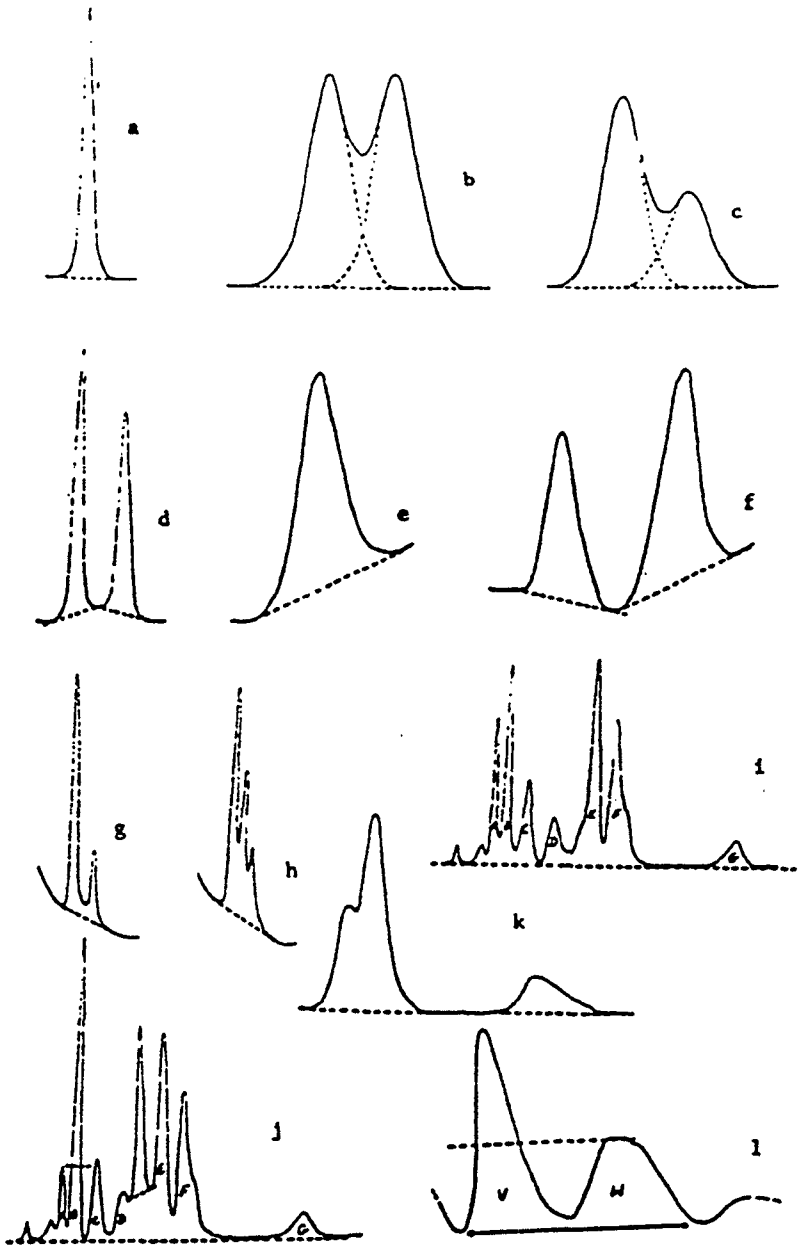

Fig. 6—Baseline construction for some typical gas chromatographic peaks. a, symmetrical separated flat baseline; b and c, overlapping flat baseline; d, separated (pen does not return to baseline between peaks); e, separated sloping baseline; f, separated (pen goes below baseline between peaks); g, α- and γ-BHC sloping baseline; h, α-, β-, and γ-BHC sloping baseline; i, chlordane flat baseline; j, heptachlor and heptachlor epoxide superimposed on chlordane; k, chair-shaped peaks, unsymmetrical peak; l, p,p'-DDT superimposed on toxaphene.

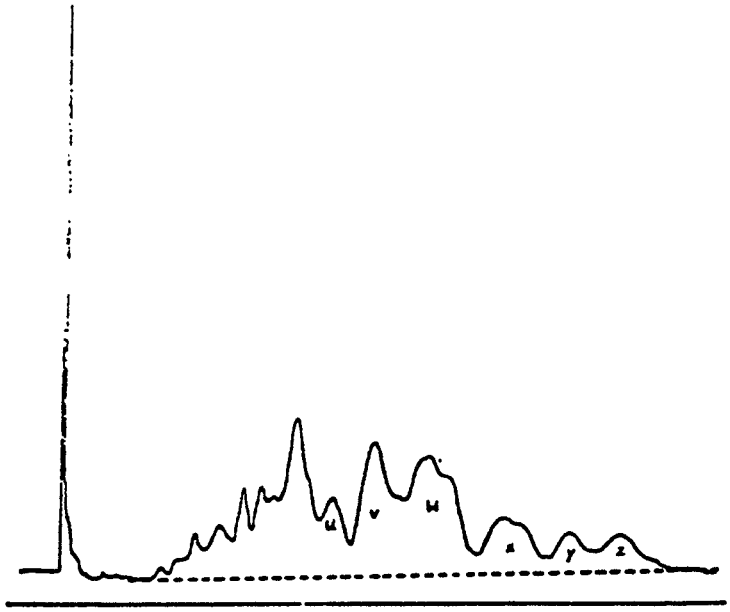

Fig. 7a--Baseline construction for multiple residues with standard toxaphene.

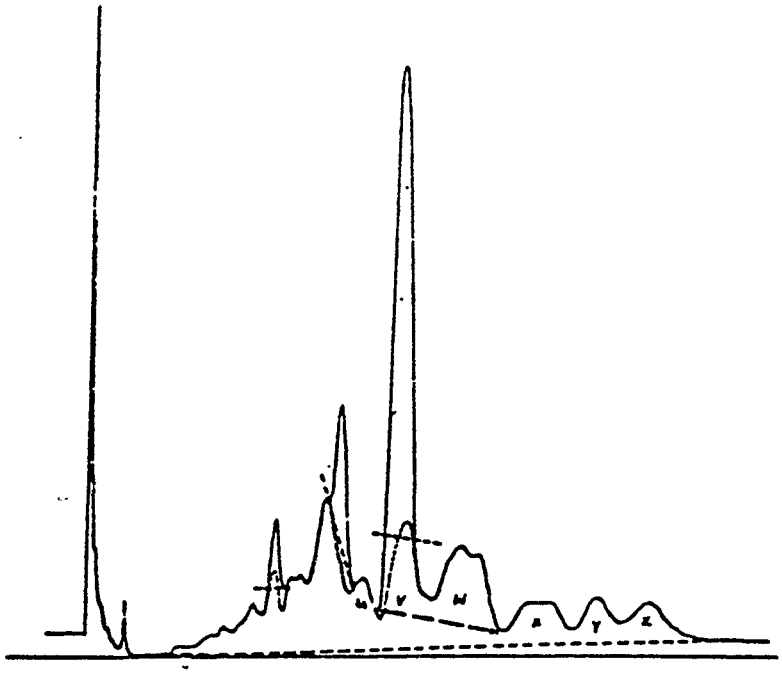

Fig. 7b--Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

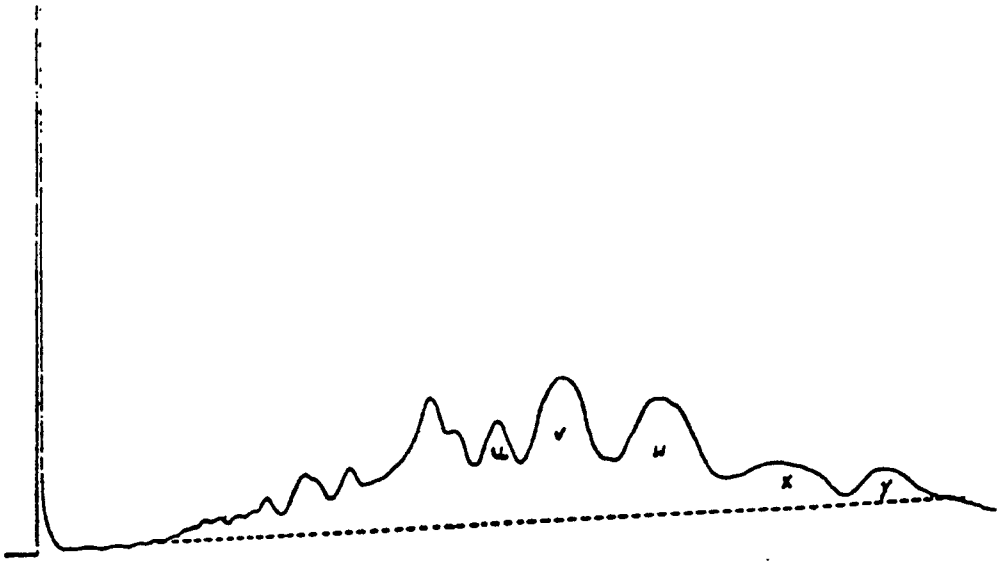

Fig. 8a--Baseline construction for multiple residues: standard toxaphene.

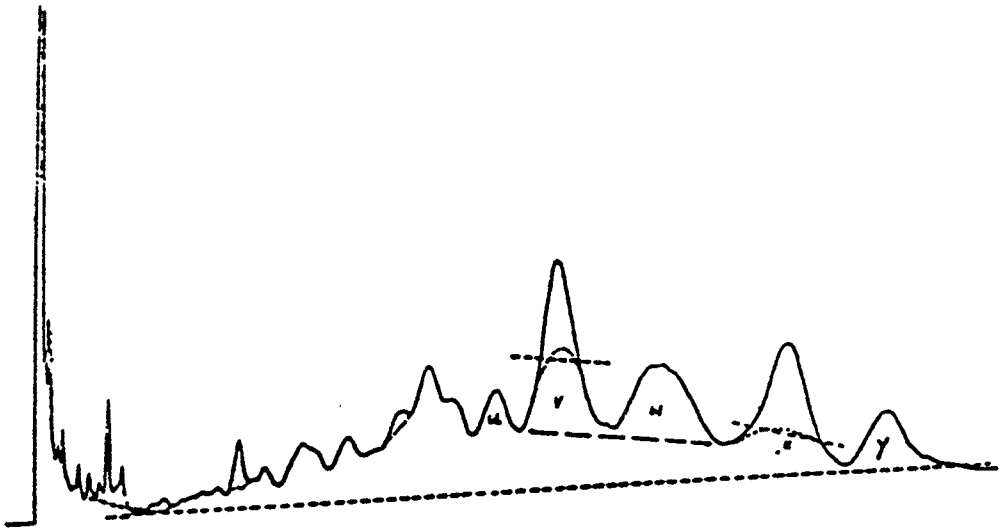

Fig. 8b--Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

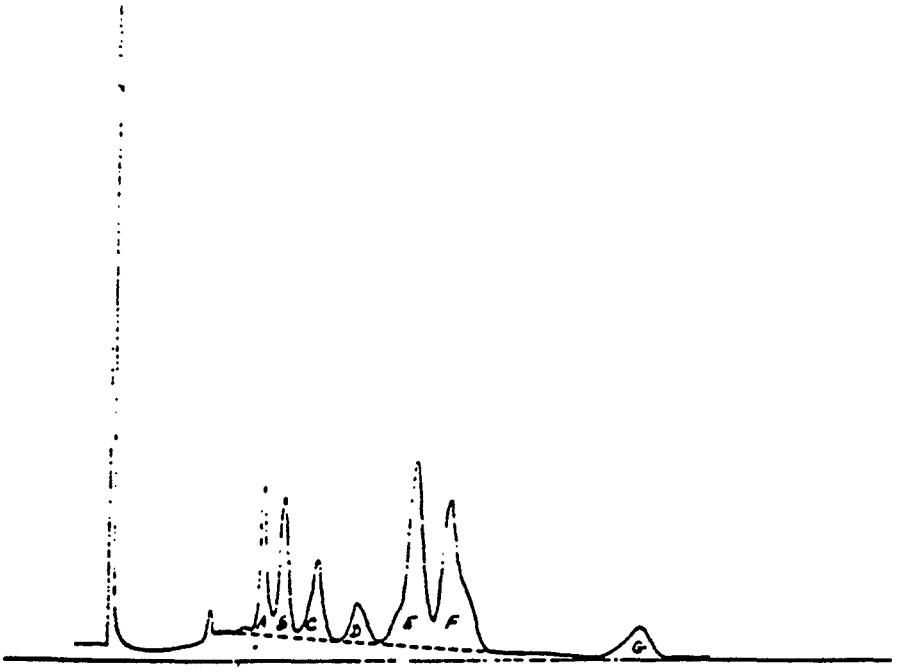

Fig. 9a--Baseline construction for multiple residues: standard chlordane.

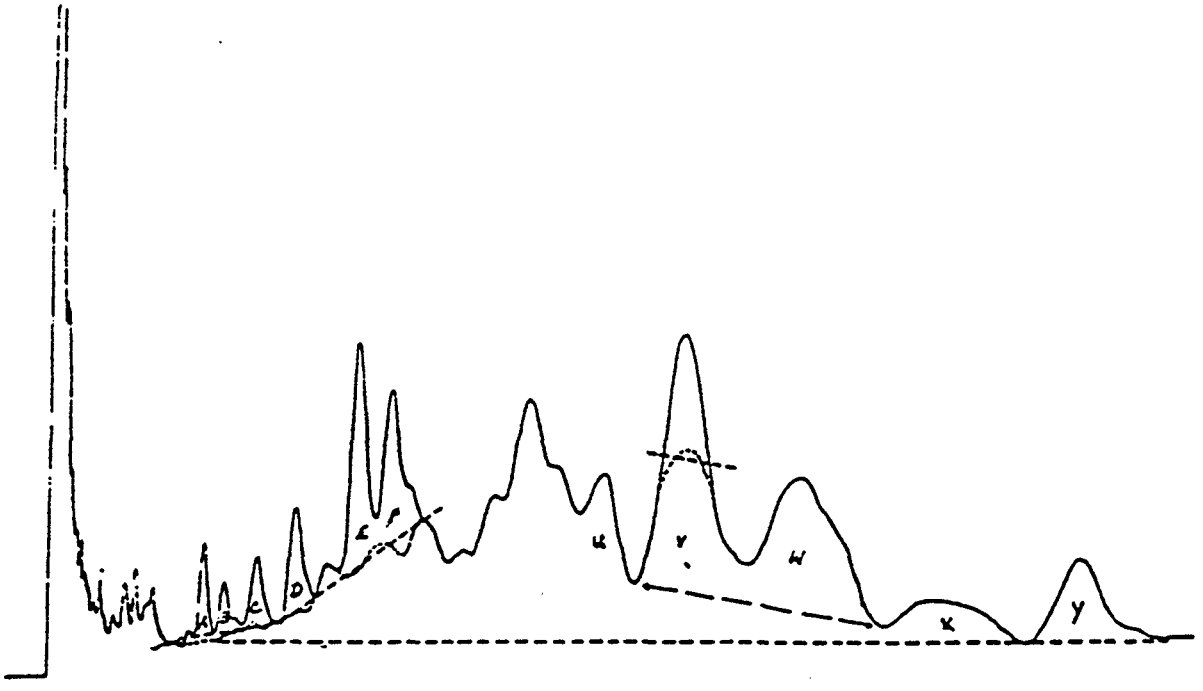

Fig. 9b—Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.

7.6.2 Toxaphene: Quantitative calculation of toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust sample size so that toxaphene major peaks are 10-30% full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within ±10 ng of the sample; (c) construct the baseline of standard toxaphene between it extremities; and (d) construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide (Figures 7, 8, and 9). This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard. A toxaphene standard that has been passed through a Florisil column will show a shorter retention time for peak X and an enlargement of peak Y.

7.6.3 Toxaphene and DDT: If DDT is present, it will superimpose itself on toxaphene peak V. To determine the approximate baseline of the DDT, draw a line connecting the trough of peaks U and V with the trough of peaks W and X and construct another line parallel to this line which will just cut the top of peak W (Figure 61). This procedure was tested with ratios of standard toxaphene-DDT mixtures from 1:10 to 2:1 and the results of added and calculated DDT and toxaphene by the "parallel lines" method of baseline construction were within 10% of the actual values in all cases.

7.6.3.1 A series of toxaphene residues have been calculated using total peak area for comparison to the standard and also using area of the last four peaks only in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram is interfered with by other substances.

7.6.3.2 The baseline for methoxychlor superimposed on toxaphene (Figure 8b) was constructed by overlaying the samples on a toxaphene standard of approximately the same concentration (Figure 8a) and viewing the charts against a lighted background.

7.6.4 Chlordane is a technical mixture of at least 11 major components and 30 or more minor ones. Gas chromatography-mass spectrometry and nuclear magnetic resonance analytical techniques have been applied to the elucidation of the chemical structures of the many chlordane constituents. Figure 9a is a chromatogram of standard chlordane. Peaks E and F are responses to trans- and cis-chlordane, respectively. These are the two major components of technical chlordane, but the exact percentage of each in the technical material is not completely defined and is not consistent from batch to batch. Other labelled peaks in Figure 9a are thought to represent: A, monochlorinated adduct of pentachlorocyclopentadiene with cyclopentadiene; B, coelution of heptachlor and α-chlordene; C, coelution of β-chlordene and γ-chlordene;

D, a chlordane analog; G, coelution of cis-nonachlor and "Compound K," a chlordane isomer. The right "shoulder" of peak F is caused by trans-nonachlor.

7.6.4.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane; plant and/or animal metabolities; and products of degradation caused by exposure to environmental factors such as water and sunlight. Only limited information is available on which residue GC patterns are likely to occur in which samples types, and even this information may not be applicable to a situation where the route of exposure is unusual. For example, fish exposed to a recent spill of technical chlordane will contain a residue drastically different from a fish whose chlordane residue was accumulated by ingestion of smaller fish or of vegetation, which in turn had accumulated residues because chlordane was in the water from agricultural runoff.

7.6.4.2 Because of this inability to predict a chlordane residue GC pattern, it is not possible to prescribe a single method for the quantitation of chlordane residues. The analyst must judge whether or not the residue's GC pattern is sufficiently similar to that of a technical chlordane reference material to use the latter as a reference standard for quantitation.

7.6.4.3 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate each peak separately against the appropriate reference materials and report the individual residues. (Reference materials are available for at least 11 chlordane constituents, metabolites or degradation products which may occur in the residue.)

7.6.4.4 When the GC pattern of the residue resembles that of technical chlordane, quantitate chlordane residues by comparing the total area of the chlordane chromatogram from peaks A through F (Figure 9a) in the sample versus the same part of the standard chromatogram. Peak G may be obscured in a sample by the presence of other pesticides. If G is not obscured, include it in the measurement for both standard and sample. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion as in Figure 6j, calculate these separately and subtract their areas from total area to give a corrected chlordane area. (Note that octachlor epoxide, metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.4.5 To measure the total area of the chlordane chromatogram, proceed as in Section 7.6.2 on toxaphene. Inject an amount of technical chlordane standard which will produce a chromatogram in which peaks E and F are approximately the same size as those in the sample chromatograms. Construct the baseline beneath the standard from the beginning of peak A to the end of peak F as shown in Figure 9a. Use the distance from the trough between peaks E and F to the baseline in the chromatogram of the standard to construct the baseline in the chromatogram of the sample. Figure 9b shows how the presence of toxaphene causes the baseline under chlordane to take an upward angle. When the size of peaks E and F in standard and sample chromatograms are the same, the distance from the trough of the peaks to the baselines should be the same. Measurement of chlordane area should be done by total peak area if possible.

NOTE: A comparison has been made of the total peak area integration method and the addition of peak heights method for several samples containing chlordane. The peak heights A, B, C, D, E, and F were measured in millimeters from peak maximum of each to the baseline constructed under the total chlordane area and were then added together. These results obtained by the two techniques are too close to ignore this method of "peak height addition" as a means of calculating chlordane. The technique has inherent difficulties because not all the peaks are symmetrical and not all are present in the same ratio in standard and in sample. This method does offer a means of calculating results if no means of measuring total area is practical.

7.6.5 **Polychlorinated biphenyls (PCBs):** Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, Strobane, and chlordane: in each case, the chemical is made up of numerous compounds and so the chromatograms are multi-peak; also in each case the chromatogram of the residue may not match that of the standard.

7.6.5.1 Mixtures of PCB of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the tradename Aroclor (1200 series and 1016). Though these Aroclors are no longer marketed, the PCBs remain in the environment and are sometime found as residues in foods, especially fish.

7.6.5.2 PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue. This may also involve a judgment about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.5.3 Quantitate PCB residues by comparing total area or height of residue peaks to total area of height of peaks from appropriate Aroclor(s) reference materials. Measure total area or height response from common baseline under all peaks. Use only those peaks from sample that can be attributed to chlorobiphenyls. These peaks must also be present in chromatogram of reference materials. Mixture of Aroclors may be required to provide best match of GC patterns of sample and reference.

7.6.6 DDT: DDT found in samples often consists of both o,p'- and p,p'-DDT. Residues of DDE and TDE are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such.

7.6.7 Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

7.6.7.1 Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the α-, γ-, and δ-isomers and 14 weeks for the β-isomer. Thus it may be possible to have any combination of the various isomers in different food commodities. BHC found in dairy products usually has a large percentage of β-isomer.

7.6.7.2 Individual isomers (α, β, γ, and δ) were injected into gas chromatographs equipped with flame ionization, microcoulometric, and electron capture detectors. Response for the four isomers is very nearly the same whether flame ionization or microcoulometric GLC is used. The α-, γ-, and δ-isomers show equal electron affinity. β-BHC shows a much weaker electron affinity compared to the others isomers.

7.6.7.3 Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer, using a GC column which separates all the isomers from one another.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; endrin, 10ug/mL; and any other single-component pesticide, 2 ug/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 ug/mL in acetone.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.4.1 The GC/MS would normally require a minimum concentration of 10 ng/uL in the final extract, for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractables extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 ug/L for single-component pesticides and from 8.5 to 400 ug/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

1. U.S. EPA, "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 10: Pesticides and PCBs," Report for EPA Contract 68-03-2605.

2. U.S. EPA, "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, October 1980.

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8. Millar, J.D., R.E. Thomas and H.J. Schattenberg, "EPA Method Study 18, Method 608: Organochlorine Pesticides and PCBs," U.S. EPA/EMSL, Research Triangle Park, NC, EPA-600/4-84-061, 1984.

9. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

10. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

11. U.S. Food and Drug Administration, Pesticide Analytical Manual, Vol. 1, June 1979.

12. Sawyer, L.D., JAOAC, 56, 1015-1023 (1973), 61 272-281 (1978), 61 282-291 (1978).

13. Official Methods of Analysis of the Association of Official Analytical Chemists, 12th Edition; Changes in Methods, JAOAC 61, 465-466 (1978), Sec. 29.018.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Aldrin	0.81C+0.04	0.16X-0.04	0.20X-0.01
α-BHC	0.84C+0.03	0.13X+0.04	0.23X-0.00
β-BHC	0.81C+0.07	0.22X+0.02	0.33X-0.95
δ-BHC	0.81C+0.07	0.18X+0.09	0.25X+0.03
γ-BHC	0.82C-0.05	0.12X+0.06	0.22X+0.04
Chlordane	0.82C-0.04	0.13X+0.13	0.18X+0.18
4,4'-DDD	0.84C+0.30	0.20X-0.18	0.27X-0.14
4,4'-DDE	0.85C+0.14	0.13X+0.06	0.28X-0.09
4,4'-DDT	0.93C-0.13	0.17X+0.39	0.31X-0.21
Dieldrin	0.90C+0.02	0.12X+0.19	0.16X+0.16
Endosulfan I	0.97C+0.04	0.10X+0.07	0.18X+0.08
Endosulfan II	0.93C+0.34	0.41X-0.65	0.47X-0.20
Endosulfan Sulfate	0.89C-0.37	0.13X+0.33	0.24X+0.35
Endrin	0.89C-0.04	0.20X+0.25	0.24X+0.25
Heptachlor	0.69C+0.04	0.06X+0.13	0.16X+0.08
Heptachlor epoxide	0.89C+0.10	0.18X-0.11	0.25X-0.08
Toxaphene	0.80C+1.74	0.09X+3.20	0.20X+0.22
PCB-1016	0.81C+0.50	0.13X+0.15	0.15X+0.45
PCB-1221	0.96C+0.65	0.29X-0.76	0.35X-0.62
PCB-1232	0.91C+10.79	0.21X-1.93	0.31X+3.50
PCB-1242	0.93C+0.70	0.11X+1.40	0.21X+1.52
PCB-1248	0.97C+1.06	0.17X+0.41	0.25X-0.37
PCB-1254	0.76C+2.07	0.15X+1.66	0.17X+3.62
PCB-1260	0.66C+3.76	0.22X-2.37	0.39X-4.86

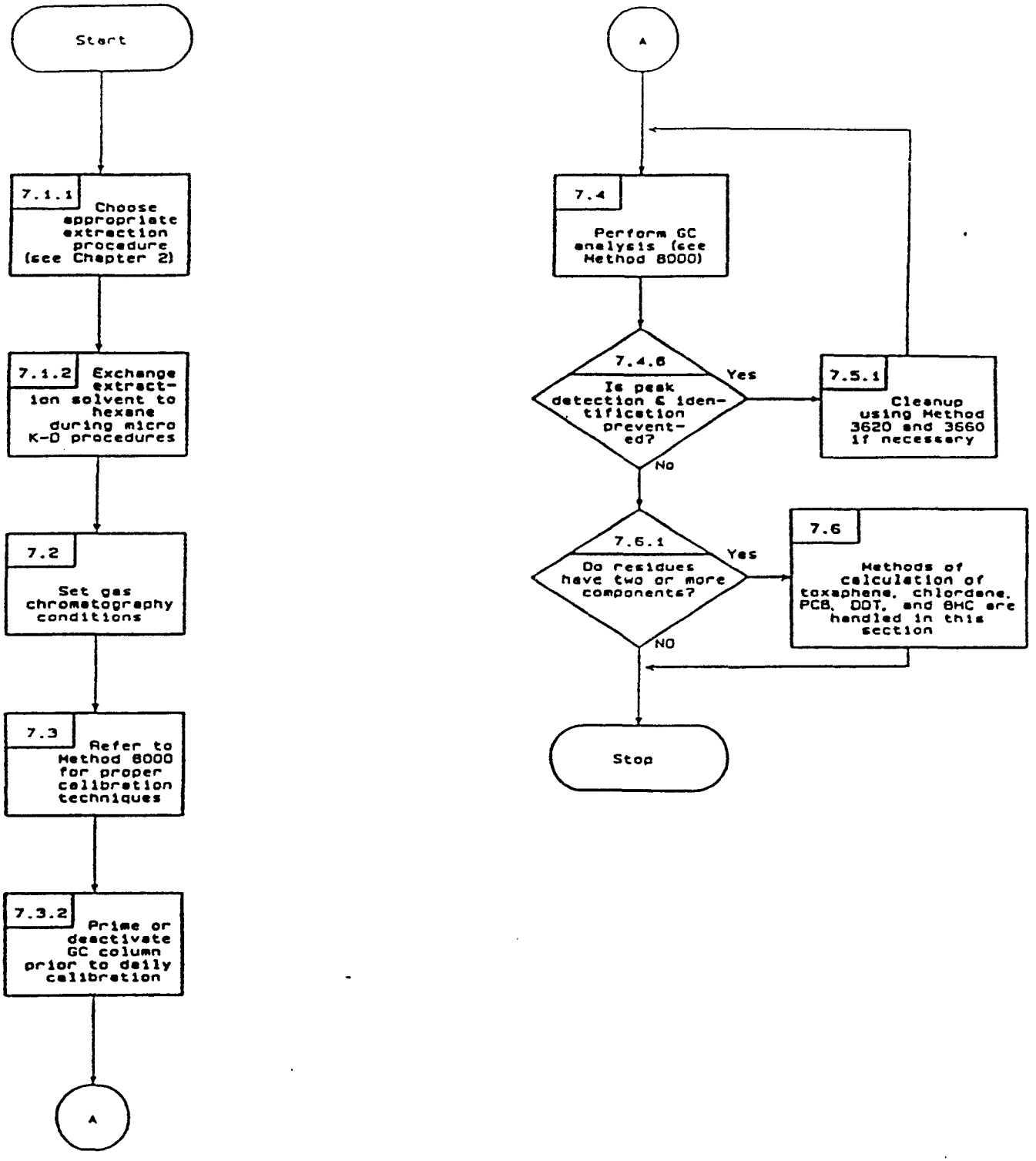
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Prime or deactivate GC column prior to daily calibration
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.6 Is peak detection & identification prevented?
Yes
7.5.1 Cleanup using Method 3620 and 3660 if necessary
No
7.6.1 Do residues have two or more components?
Yes
7.6 Methods of calculation of toxaphene, chlordane, PCB, DDT, and BHC are handled in this section
NO
Stop

300623

METHOD 8240

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.2 Method 8240 can be used to quantify most volatile organic compounds that have boiling points below 200°C [vapor pressure is approximately equal to mm Hg @ 25°C] and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique, however, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The practical quantitation limit (PQL) of Method 8240 for an individual compound is approximately 5 ug/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 ug/L for ground water (see Table 2). PQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

300624

TABLE 1. RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Acetone	--	43	58
Acrolein	--	56	55, 58
Acrylonitrile	--	53	52, 51
Benzene	17.0	78	52, 77
Bromochloromethane (I.S.)	9.3	128	49, 130, 51
Bromodichloromethane	14.3	83	85, 129
4-Bromofluorobenzene (surr.)	28.3	95	174, 176
Bromoform	19.8	173	171, 175, 252
Bromomethane	3.1	94	96, 79
2-Butanone	--	72	57, 43
Carbon disulfide	--	76	78
Carbon tetrachloride	13.7	117	119, 121
Chlorobenzene	24.6	112	114, 77
Chlorobenzene-d_5 (I.S.)	--	117	82, 119
Chlorodibromomethane	--	129	208, 206
Chloroethane	4.6	64	66, 49
2-Chloroethyl vinyl ether	18.6	63	65, 106
Chloroform	11.4	83	85, 47
Chloromethane	2.3	50	52, 49
Dibromomethane	--	93	174, 95
1,4-Dichloro-2-butane	--	75	53, 89
Dichlorodifluoromethane	--	85	87, 50, 101
1,1-Dichloroethane	--	63	65, 83
1,2-Dichloroethane	10.1	62	64, 98
1,2-Dichloroethane-d_4 (surr.)	12.1	65	102
1,1-Dichloroethene	9.0	96	61, 98
trans-1,2-Dichloroethene	10.0	96	61, 98
1,2-Dichloropropane	15.7	63	62, 41
cis-1,3-Dichloropropene	15.9	75	77, 39
trans-1,3-Dichloropropene	17.2	75	77, 39
1,4-Difluorobenzene (I.S.)	19.6	114	63, 88
Ethanol	--	31	45, 27, 46
Ethylbenzene	26.4	106	91
Ethyl methacrylate	--	69	41, 39, 99
2-Hexanone	--	43	58, 57, 100
Iodomethane	--	142	127, 141
Methylene chloride	6.4	84	49, 51, 86
4-Methyl-2-pentanone	--	43	58, 100
Styrene	--	104	78, 103
1,1,2,2-Tetrachloroethane	22.1	83	85, 131, 133
Tetrachloroethene	22.2	164	129, 131, 166
Toluene	23.5	92	91, 65
Toluene-d_8 (surr.)	--	98	70, 100

TABLE 1. - Continued

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
1,1,1-Trichloroethane	13.4	97	99, 117
1,1,2-Trichloroethane	17.2	97	83, 85, 99
Trichloroethene	16.5	130	95, 97, 132
Trichlorofluoromethane	8.3	101	103, 66
1,2,3-Trichloropropane	--	75	110, 77, 61
Vinyl acetate	--	43	86
Vinyl chloride	3.8	62	64, 61
Xylene	--	106	91

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TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR VOLATILE ORGANICS[a]

Volatiles	CAS Number	Practical Quantitation Limits[b] Ground water ug/L	Low Soil/Sediment ug/Kg
1. Chloromethane	74-87-3	10	10
2. Bromomethane	74-83-9	10	10
3. Vinyl Chloride	75-01-4	10	10
4. Chloroethane	75-00-3	10	10
5. Methylene Chloride	75-09-2	5	5
6. Acetone	67-64-1	100	100
7. Carbon Disulfide	75-15-0	5	5
8. 1,1-Dichloroethene	75-35-4	5	5
9. 1,1-Dichloroethane	75-35-3	5	5
10. trans-1,2-Dichloroethene	156-60-5	5	5
11. Chloroform	67-66-3	5	5
12. 1,2-Dichloroethane	107-06-2	5	5
13. 2-Butanone	78-93-3	100	100
14. 1,1,1-Trichloroethane	71-55-6	5	5
15. Carbon Tetrachloride	56-23-5	5	5
16. Vinyl Acetate	108-05-4	50	50
17. Bromodichloromethane	75-27-4	5	5
18. 1,1,2,2-Tetrachloroethane	79-34-5	5	5
19. 1,2-Dichloropropane	78-87-5	5	5
20. trans-1,3-Dichloropropene	10061-02-6	5	5
21. Trichloroethene	79-01-6	5	5
22. Dibromochloromethane	124-48-1	5	5
23. 1,1,2-Trichloroethane	79-00-5	5	5
24. Benzene	71-43-2	5	5
25. cis-1,3-Dichloropropene	10061-01-5	5	5
26. 2-Chloroethyl Vinyl Ether	110-75-8	10	10
27. Bromoform	75-25-2	5	5
28. 2-Hexanone	591-78-6	50	50
29. 4-Methyl-2-pentanone	108-10-1	50	50
30. Tetrachloroethene	127-18-4	5	5

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TABLE 2. - Continued

Volatiles	CAS Number	Practical Quantitation Limits[b] Ground water ug/L	Low Soil/Sediment ug/Kg
31. Toluene	108-88-3	5	5
32. Chlorobenzene	108-90-7	5	5
33. Ethyl Benzene	100-41-4	5	5
34. Styrene	100-42-5	5	5
35. Total Xylenes		5	5

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable. See the following information for further guidance on matrix-dependent PQLs.

[b]PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, PQLs will be higher, based on the % moisture in each sample.

Other Matrices:	Factor[1]
Water miscible liquid waste	50
High-level soil & sludges	125
Non-water miscible waste	500

[1]PQL = [PQL for ground water (Table 2)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

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2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 The purge-and-trap process: An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of reagent water to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes: 10-uL, 25-uL, 100-uL, 250-uL, 500-uL, and 1,000 uL. These syringes should be equipped with a 20-gauge (0.006-in I.D.) needle

having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve: Two-way, with luer ends (three each), if applicable to the purging device.

4.3 Syringe: 5-mL, gas-tight with shutoff valve.

4.4 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.5 Glass scintillation vials: 20-mL, with screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

4.6 Volumetric flasks: 10-mL and 100-mL, class A with ground-glass stoppers.

4.7 Vials: 2-mL, for GC autosampler.

4.8 Spatula: Stainless steel.

4.9 Disposable pipets: Pasteur.

4.10 Heater or heated oil bath: Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3-mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated

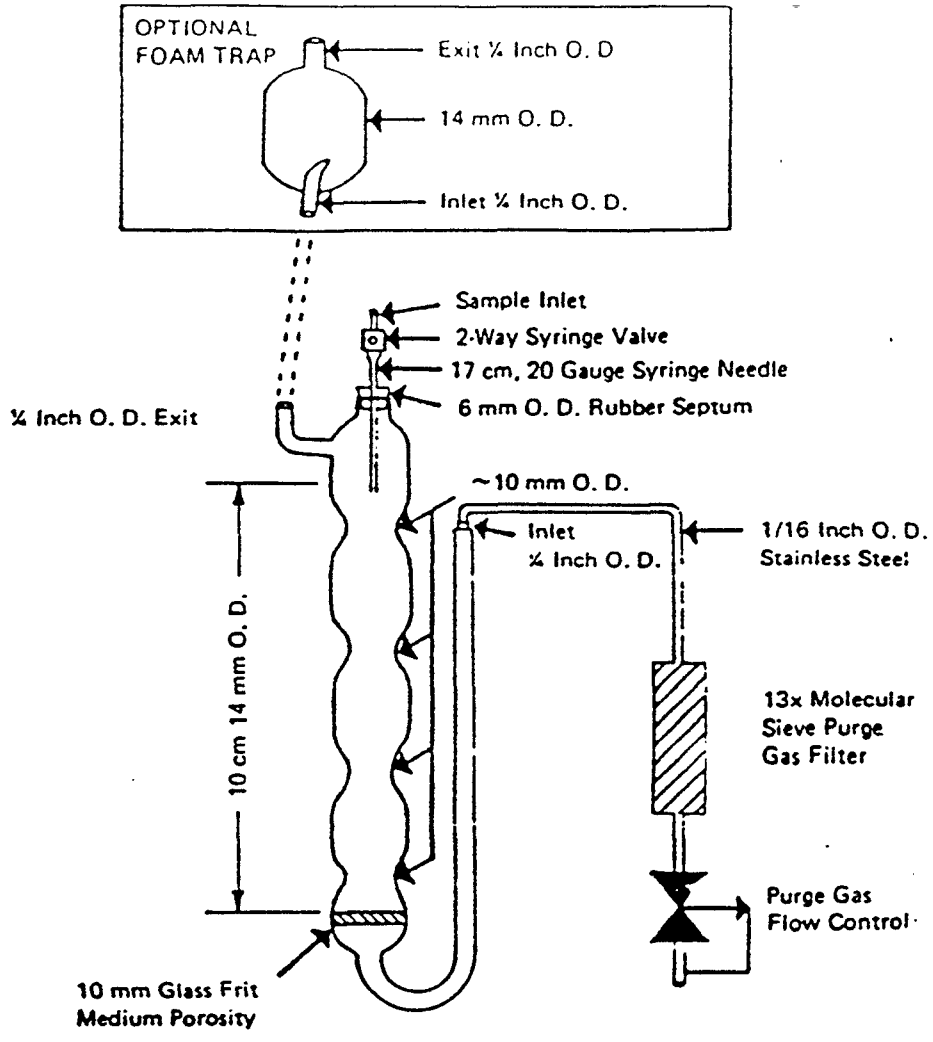

Figure 1. Purging chamber.

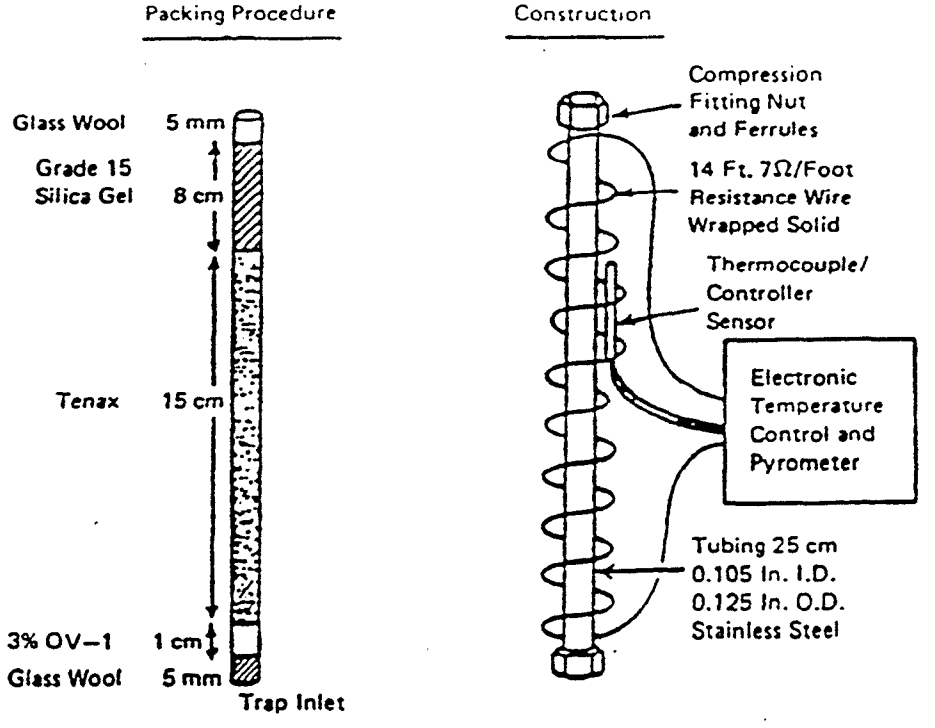

Figure 2. Trap packings and construction to include desorb capability for Method 8240.

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and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 Trap Packing Materials:

4.11.5.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.11.5.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.11.5.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

4.12 Gas chromatograph/mass spectrometer system:

4.12.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.12.2 Column: 6-ft x 0.1-in. I.D. glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 Mass spectrometer: Capable of scanning from 35-260 amu every 3 sec or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of

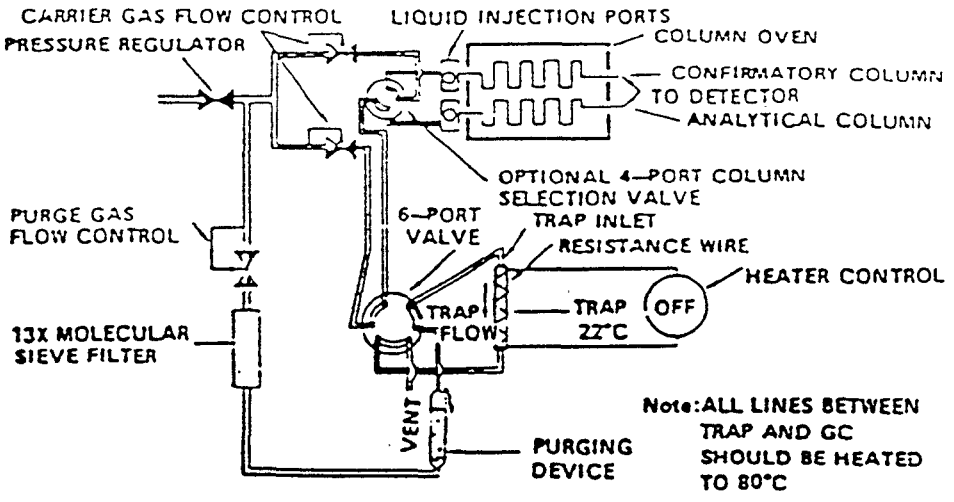

Figure 3. Schematic of purge-and-trap device — purge mode for Method 8240.

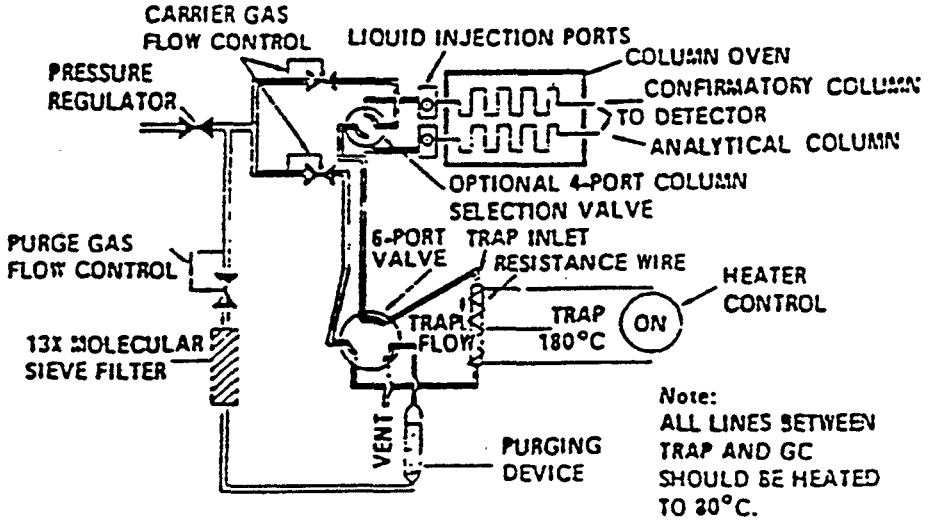

Figure 4. Schematic of purge-and-trap device — desorb mode for Method 8240.

TABLE 3. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.12.5 Data system: A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

5.0 REAGENTS

5.1 Stock solutions: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.1.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.1.2 Add the assayed reference material, as described below.

5.1.2.1 Liquids: Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.1.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.1.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.4 Transfer the stock standard solution into a Teflon-sealed screw cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.1.5 Prepare fresh standards every two months for gases. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.2 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3 Surrogate standards: The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.1, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 ug/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 uL of the surrogate spiking solution prior to analysis.

5.4 Internal standards: The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.1 and 5.2. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 ug/mL of each internal standard compound. Addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 ug/L.

5.5 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/uL of BFB in methanol should be prepared.

5.6 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Sections 5.1 and 5.2). Prepare these solutions in reagent water. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). Store for one week only in a vial with no headspace.

5.7 Matrix spiking standards: Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene,

trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 ug/10.0 mL.

5.8 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored at -10°C to -20°C in screw-cap amber bottles with Teflon liners.

5.9 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.9.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.9.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.9.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hr. While it is still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.10 Methanol: Pesticide quality or equivalent. Store apart from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.2 Initial calibration for purge-and-trap procedure:

7.2.1 Recommended GC/MS operating conditions:

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak but not to exceed 7 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 min.
Column temperature program:	8°C/min.
Final column temperature:	220°C.
Final column holding time:	15 min.
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.2.2 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection or purging of 4-bromofluorobenzene (2-uL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Section 4.11. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of reagent water to the purging device. The reagent water is added to the purging device using a 5-mL glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-uL or 25-uL micro-syringe equipped with a long needle (Paragraph 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Paragraph 5.6). Add the aliquot of calibration solution directly to the reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 10 uL of the internal standard solution (Paragraph 5.4). Close the 2-way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Section 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Section 7.5.2). The RF is calculated as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_x = Concentration of the compound being measured.

7.2.8 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.2.8.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.8.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

7.2.8.3 Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.9 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs).

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

RSD = relative standard deviation.

$\bar{x}$ = mean of 5 initial RFs for a compound.

SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The %RSD for each individual CCC should be less than 30 percent. This criterion must be met in order for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.3 Daily GC/MS calibration:

7.3.1 Prior to the analysis of samples, inject or purge 50-ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hr shift.

7.3.2 The initial calibration curve (Section 7.2) for each compound of interest must be checked and verified once every 12 hr of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Paragraph 7.3.3) and CCC (Paragraph 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs): A system performance check must be made each 12 hr. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Paragraph 7.2.9 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_C}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_C = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (>25% difference), for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins.

7.3.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis:

7.4.1 Water samples:

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are: the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (ECD); and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Paragraph 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Section 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Section 7.2.8).

7.4.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hr. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10-to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Paragraph 7.4.1.6 into the flask. Aliquots of less than 1-mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5-mL syringe with the diluted sample as i n Paragraph 7.4.1.6.

7.4.1.8 Add 10.0 uL of surrogate spiking solution (Paragraph 5.3) and 10 uL of internal standard spiking solution (Paragraph 5.4) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.4.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.10 Close both valves and purge the sample for 11.0 $\pm$ 0.1 min at ambient temperature.

7.4.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for 4 min. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5-mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 min, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank reagent water analysis. If the blank

analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.15 For matrix spike analysis, add 10 uL of the matrix spike solution (Paragraph 5.7) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.4.1.16 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Sections 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water-miscible liquids:

7.4.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with reagent water.

7.4.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100-mL volumetric flask and diluting to volume with reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with reagent water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples: It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-level method (0.005-1 mg/kg) or the high-level method (>1 mg/kg).

7.4.3.1 Low-level method: This is designed for samples containing individual purgeable compounds of <1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5-g sample if the expected concentration is <0.1 mg/kg or a 1-g sample for expected concentrations between 0.1 and 1 mg/kg.

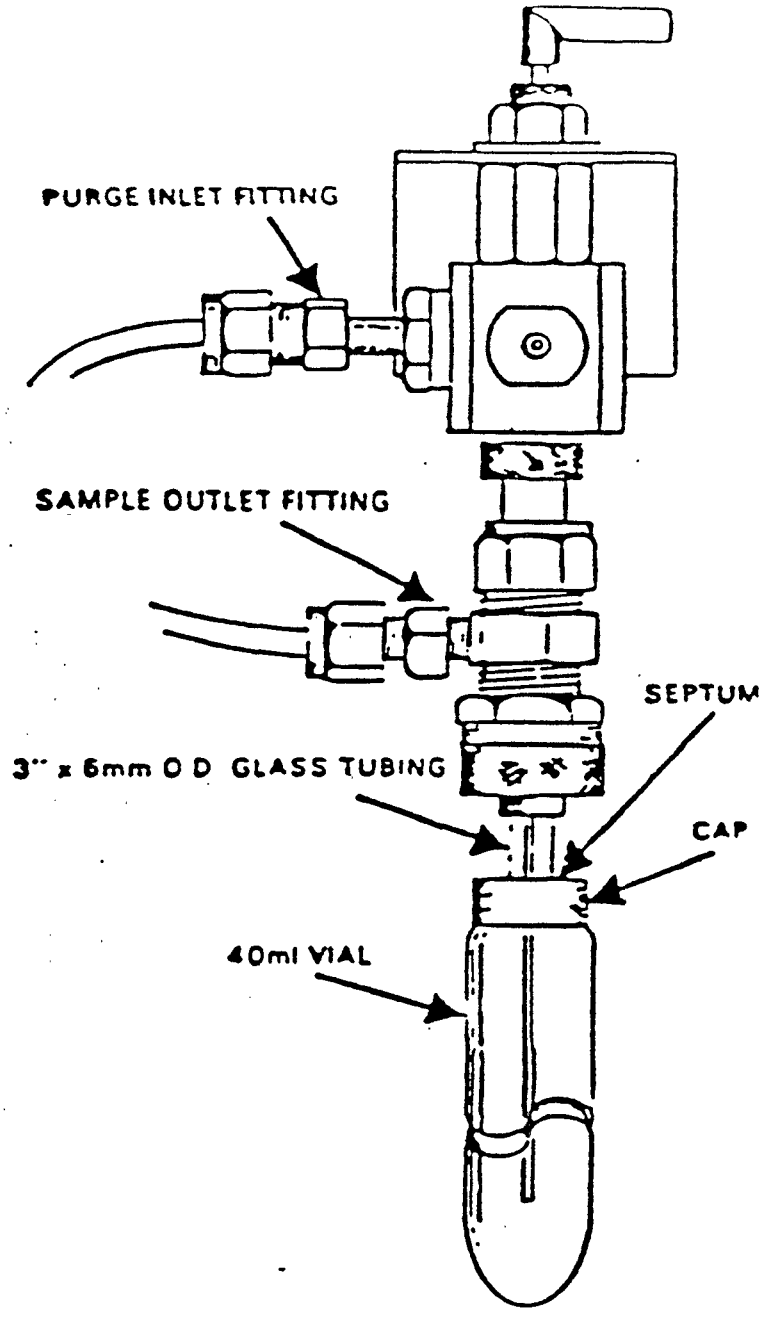

Figure 5. Lou Soils Impinger

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7.4.3.1.2 The GC/MS system should be set up as in Paragraphs 7.4.1.2-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of surrogate spiking solution (Paragraph 5.3) and internal standard solution (Paragraph 5.4) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 uL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 ug/kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Paragraph 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent moisture of the soil/sediment sample. This includes waste samples that are amenable to moisture determination. Other wastes should be reported on a wet-weight basis. Immediately after weighing the sample, weigh (to 0.1 g) 5-10 g of additional sediment/soil into a tared crucible. Dry the contents of the crucibles overnight at 105°C. Allow to cool in a desiccator and reweigh the dried contents. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\% \text{ moisture} = \frac{\text{grams of sample - grams of dry sample}}{\text{grams of sample}} \times 100$$

7.4.3.1.6 Add the spiked reagent water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Paragraphs 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.4.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 min.

7.4.3.1.8 Proceed with the analysis as outlined in Paragraphs 7.4.1.11-7.4.1.16. Use 5 mL of the same reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1-g sample were analyzed, the medium-level method must be followed.

7.4.3.1.9 For low-level sediment/soils add 10 uL of the matrix spike solution (Paragraph 5.7) to the 5 mL of water (Paragraph 7.4.3.1.3). The concentration for a 5-g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.4.3.2 High-level method: The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. An aliquot of the extract is added to reagent water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol weigh 4 g (wet weight) of sample into a tared 20-mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent moisture of the sample using the procedure in Paragraph 7.4.3.1.5. For waste that is soluble in methanol, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of methanol into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min.

NOTE: Steps 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of reagent methanol to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100-uL aliquot of each of these extracts in Paragraph 7.4.3.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Paragraphs 7.4.1.2-7.4.1.4. This should be done prior to the addition of the methanol extract to reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a medium-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 uL of internal standard solution. Also add the volume of methanol extract determined in Paragraph 7.4.3.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Paragraphs 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 uL of methanol to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the medium-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Paragraph 5.3), and 1.0 mL of matrix spike solution (Paragraph 5.7) as in Paragraph 7.4.3.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4-g sample. Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Paragraph 7.4.3.2.6).

TABLE 4. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF MEDIUM-LEVEL SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 ug/kg	100 uL
1,000-20,000 ug/kg	50 uL
5,000-100,000 ug/kg	10 uL
25,000-500,000 ug/kg	100 uL of 1/50 dilution [b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a]The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

[b]Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.5 Data interpretation:

7.5.1 Qualitative analysis:

7.5.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.5.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hr as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.5.1.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum). (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis:

7.5.2.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.2.7).

V_o = Volume of water purged (mL), taking into consideration any dilutions made.

TABLE 5. VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromoform
Bromomethane	2-Butanone
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	2-Chloroethyl vinyl ether
Chloromethane	Dibromomethane
Dichlorodifluoromethane	1,4-Dichloro-2-butene
1,1-Dichloroethane	1,2-Dichloropropane
1,2-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	trans-1,3-Dichloropropene
1,1-Dichloroethene	1,1,1-Trichloroethane
trans-1,2-Dichloroethene	1,1,2-Trichloroethane
Iodomethane	Trichloroethene
Methylene chloride	Vinyl acetate
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

Sediment/Soil, Sludge, and Waste:

High-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = same as for water.

V_t = volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made).

V_i = volume of extract added (uL) for purging.

W_s = weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.5.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The % moisture of the sample (as calculated in Paragraph 7.4.3.1.5) should be reported along with the data in either instance.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.5 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing

analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Section 7.2.2.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.3.3 and the CCC criteria in 7.3.4, each 12 hr.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 10 ug/mL in methanol. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Prepare a QC check sample to contain 20 ug/L of each analyte by adding 200 uL of QC check sample concentrate to 100 mL of reagent water.

8.5.3 Four 5-mL aliquots of the well-mixed QC check sample are analyzed according to the method beginning in Section 7.4.1.

8.5.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte using the four results.

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Paragraph 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike duplicate/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a specific limit, the spike should be at 20 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

TABLE 6. CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in ug/L.
s = Standard deviation of four recovery measurements, in ug/L.
$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.
p, p_s = Percent recovery measured.
D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 ug/L. These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

8.6.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be acounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for X; (3) calculate the range for recovery at the spike concentration as (100x'/T) $\pm$ 2.44(100S'/T)%.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Sectin 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC check standard by adding 10 uL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 5 mL of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyze the QC check standard to determine the concentration measured (A) of each analyte. Calculate each precent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Benzene	0.93C+2.00	0.26X-1.74	0.25X-1.33
Bromodichloromethane	1.03C-1.58	0.15X+0.59	0.20X+1.13
Bromoform	1.18C-2.35	0.12X+0.34	0.17X+1.38
Bromomethane	1.00C	0.43X	0.58X
Carbon tetrachloride	1.10C-1.68	0.12X+0.25	0.11X+0.37
Chlorobenzene	0.98C+2.28	0.16X-0.09	0.26X-1.92
Chloroethane	1.18C+0.81	0.14X+2.78	0.29X+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62X	0.84X
Chloroform	0.93C+0.33	0.16X+0.22	0.18X+0.16
Chloromethane	1.03C-1.81	0.37X+2.14	0.58X+0.43
Dibromochloromethane	1.01C-0.03	0.17X-0.18	0.17X+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22X-1.45	0.30X-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14X-0.48	0.18X-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22X-1.45	0.30X-1.20
1,1-Dichloroethane	1.05C+0.36	0.13X-0.05	0.16X+0.47
1,2-Dichloroethane	1.02C+0.45	0.17X-0.32	0.21X-0.38
1,1-Dichloroethene	1.12C+0.61	0.17X+1.06	0.43X-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14X+0.09	0.19X+0.17
1,2-Dichloropropane[a]	1.00C	0.33X	0.45X
cis-1,3-Dichloropropene[a]	1.00C	0.38X	0.52X
trans-1,3-Dichloropropene[a]	1.00C	0.25X	0.34X
Ethyl benzene	0.98C+2.48	0.14X+1.00	0.26X-1.72
Methylene chloride	0.87C+1.88	0.15X+1.07	0.32X+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16X+0.69	0.20X+0.41
Tetrachloroethene	1.06C+0.60	0.13X-0.18	0.16X-0.45
Toluene	0.98C+2.03	0.15X-0.71	0.22X-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12X-0.15	0.21X-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14X+0.02	0.18X+0.00
Trichloroethene	1.04C+2.27	0.13X+0.36	0.12X+0.59
Trichlorofluoromethane	0.99C+0.39	0.33X-1.48	0.34X-0.39
Vinyl chloride	1.00C	0.48X	0.65X

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration of X, in ug/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of X, in ug/L.
C = True value for the concentration, in ug/L.
X = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a]Estimates based upon the performance in a single laboratory.
[b]Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = $p + 3s$
Lower Control Limit (LCL) = $p - 3s$

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 624," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

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5. Budde, W.L. and J.W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April 1980.

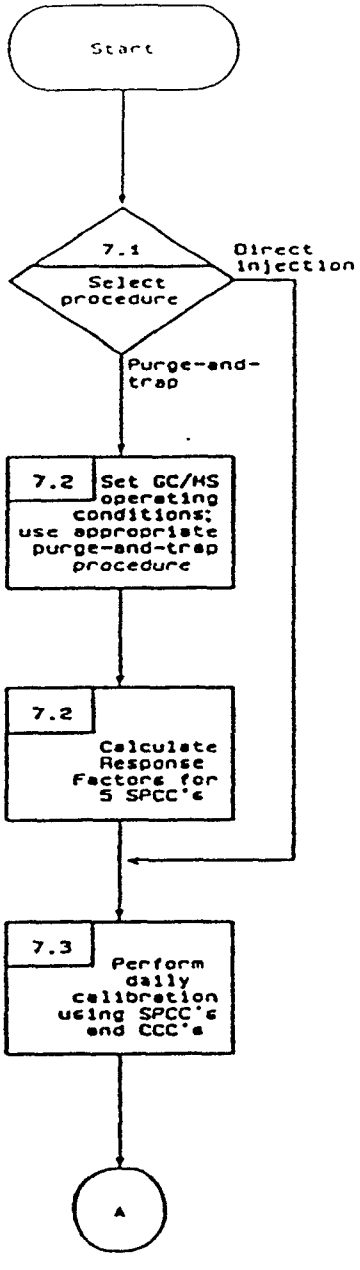
6. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

7. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

8. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

9. "Interlaboratory Method Study for EPA Method 624-Purgeables," Final Report for EPA Contract 68-03-3102.

10. "Method Performance Data for Method 624," Memorandum from R. Slater and T. Pressley, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 17, 1984.


Start
7.1
Select procedure
Direct injection
Purge-and-trap
7.2
Set GC/MS operating conditions; use appropriate purge-and-trap procedure
7.2
Calculate Response Factors for 5 SPCC's
7.3
Perform daily calibration using SPCC's and CCC's
A

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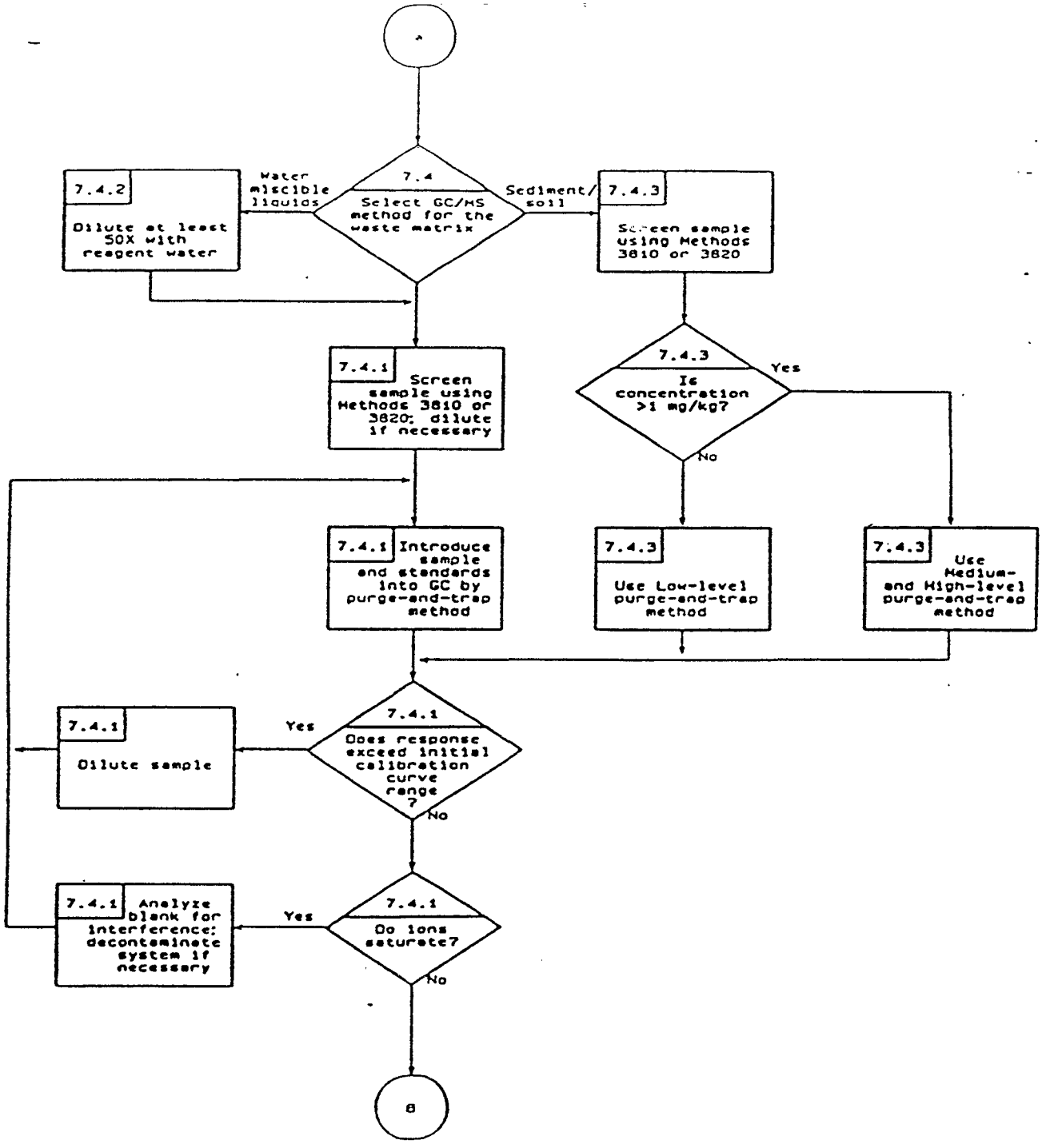
A
7.4
Select GC/MS method for the waste matrix
Water miscible liquids
Sediment/ soil
7.4.2
Dilute at least 50X with reagent water
7.4.3
Screen sample using Methods 3810 or 3820
7.4.1
Screen sample using Methods 3810 or 3820; dilute if necessary
7.4.3
Is concentration >1 mg/kg?
Yes
No
7.4.1 Introduce sample and standards into GC by purge-and-trap method
7.4.3
Use Low-level purge-and-trap method
7.4.3
Use Medium- and High-level purge-and-trap method
7.4.1
Does response exceed initial calibration curve range ?
Yes
No
7.4.1
Dilute sample
7.4.1
Do ions saturate?
Yes
No
7.4.1 Analyze blank for interference; decontaminate system if necessary
B

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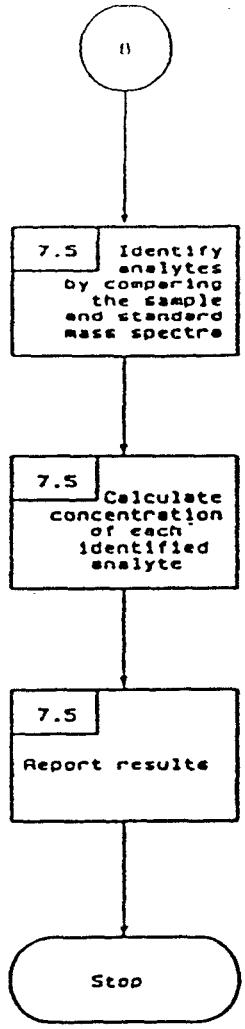
B
7.5
Identify analytes by comparing the sample and standard mass spectra
7.5
Calculate concentration of each identified analyte
7.5
Report results
Stop

300666

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The practical quantitation limit (PQL) of Method 8270 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 ug/L for ground water samples (see Table 2). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Acenaphthene	15.13	154	153, 152
Acenaphthene-d_{10} (I.S.)	15.05	164	162, 160
Acenaphthylene	14.57	152	151, 153
Acetophenone	7.96[a]	105	77, 51
Aldrin	--	66	263, 220
Aniline	5.68	93	66, 65
Anthracene	19.77	178	176, 179
4-Aminobiphenyl	19.18[a]	169	168, 170
Aroclor-1016	--	222	260, 292
Aroclor-1221	--	190	224, 260
Aroclor-1232	--	190	224, 260
Aroclor-1242	--	222	256, 292
Aroclor-1248	--	292	362, 326
Aroclor-1254	--	292	362, 326
Aroclor-1260	--	360	362, 394
Benzidine	23.87	184	92, 185
Benzoic acid	9.38	122	105, 77
Benzo(a)anthracene	27.83	228	229, 226
Benzo(b)fluoranthene	31.45	252	253, 125
Benzo(k)fluoranthene	31.55	252	253, 125
Benzo(g,h,i)perylene	41.43	276	138, 277
Benzo(a)pyrene	32.80	252	253, 125
Benzyl alcohol	6.78	108	79, 77
α-BHC	--	183	181, 109
β-BHC	--	181	183, 109
δ-BHC	--	183	181, 109
γ-BHC (Lindane)	--	183	181, 109
Bis(2-chloroethoxy)methane	9.23	93	95, 123
Bis(2-chloroethyl)ether	5.82	93	63, 95
Bis(2-chloroisopropyl)ether	7.22	45	77, 121
Bis(2-ethylhexyl)phthalate	28.47	149	167, 279
4-Bromophenyl phenyl ether	18.27	248	250, 141
Butyl benzyl phthalate	26.43	149	91, 206
Chlordane	--	373	375, 377
4-Chloroaniline	10.08	127	129
1-Chloronaphthalene	13.65[a]	162	127, 164
2-Chloronaphthalene	13.30	162	127, 164
4-Chloro-3-methylphenol	11.68	107	144, 142
2-Chlorophenol	5.97	128	64, 130
4-Chlorophenyl phenyl ether	16.78	204	206, 141
Chrysene	27.97	228	226, 229
Chrysene-d_{12} (I.S.)	27.88	240	120, 236
4,4'-DDD	--	235	237, 165
4,4'-DDE	--	246	248, 176

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
4,4'-DDT	--	235	237, 165
Dibenz(a,j)acridine	32.55[a]	279	280, 277
Dibenz(a,h)anthracene	39.82	278	139, 279
Dibenzofuran	15.63	168	139
Di-n-butylphthalate	21.78	149	150, 104
1,3-Dichlorobenzene	6.27	146	148, 111
1,4-Dichlorobenzene	6.40	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	6.35	152	150, 115
1,2-Dichlorobenzene	6.85	146	148, 111
3,3'-Dichlorobenzidine	27.88	252	254, 126
2,4-Dichlorophenol	9.48	162	164, 98
2,6-Dichlorophenol	10.05[a]	162	164, 98
Dieldrin	--	79	263, 279
Diethylphthalate	16.70	149	177, 150
p-Dimethylaminoazobenzene	24.48[a]	120	225, 77
7,12-Dimethylbenz(a)anthracene	29.54[a]	256	241, 257
α-,α-Dimethylphenethylamine	9.51[a]	58	91, 42
2,4-Dimethylphenol	9.03	122	107, 121
Dimethylphthalate	14.48	163	194, 164
4,6-Dinitro-2-methylphenol	17.05	198	51, 105
2,4-Dinitrophenol	15.35	184	63, 154
2,4-Dinitrotoluene	15.80	165	63, 89
2,6-Dinitrotoluene	14.62	165	63, 89
Diphenylamine	17.54[a]	169	168, 167
1,2-Diphenylhydrazine	--	77	105, 182
Di-n-octylphthalate	30.48	149	167, 43
Endosulfan I	--	195	339, 341
Endosulfan II	--	337	339, 341
Endosulfan sulfate	--	272	387, 422
Endrin	--	263	82, 81
Endrin aldehyde	--	67	345, 250
Endrin ketone	--	317	67, 319
Ethyl methanesulfonate	5.33[a]	79	109, 97
Fluoranthene	23.33	202	101, 203
Fluorene	16.70	166	165, 167
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64
Heptachlor	--	100	272, 274
Heptachlor epoxide	--	353	355, 351
Hexachlorobenzene	18.65	284	142, 249
Hexachlorobutadiene	10.43	225	223, 227
Hexachlorocyclopentadiene	12.60	237	235, 272
Hexachloroethane	7.65	117	201, 199
Indeno(1,2,3-cd)pyrene	39.52	276	138, 227

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Isophorone	8.53	82	95, 138
Methoxychlor	--	227	228
3-Methylcholanthrene	31.14[a]	268	253, 267
Methyl methanesulfonate	4.32[a]	80	79, 65
2-Methylnaphthalene	11.87	142	141
2-Methylphenol (o-cresol)	7.22	108	107, 79
4-Methylphenol (p-cresol)	7.60	108	107, 79
Naphthalene	9.82	128	129, 127
Naphthalene-d_8 (I.S.)	9.75	136	68
1-Naphthylamine	15.80[a]	143	115, 116
2-Naphthylamine	16.00[a]	143	115, 116
2-Nitroaniline	13.75	65	92, 138
3-Nitroaniline	15.02	138	108, 92
4-Nitroaniline	16.90	138	108, 92
Nitrobenzene	7.87	77	123, 65
Nitrobenzene-d_5 (surr.)	--	82	128, 54
2-Nitrophenol	8.75	139	109, 65
4-Nitrophenol	15.80	139	109, 65
N-Nitroso-di-n-butylamine	10.99[a]	84	57, 41
N-Nitrosodimethylamine	--	42	74, 44
N-Nitrosodiphenylamine	17.17	169	168, 167
N-Nitrosodipropylamine	7.55	70	42, 101, 130
N-Nitrosopiperidine	--	42	114, 55
Pentachlorobenzene	15.64[a]	250	252, 248
Pentachloronitrobenzene	19.47[a]	295	237, 142
Pentachlorophenol	19.25	266	264, 268
Perylene-d_{12} (I.S.)	33.05	264	260, 265
Phenacetin	18.59[a]	108	109, 179
Phenanthrene	19.62	178	179, 176
Phenanthrene-d_{10} (I.S.)	19.55	188	94, 80
Phenol	5.77	94	65, 66
Phenol-d_6 (surr.)	--	99	42, 71
2-Picoline	3.75[a]	93	66, 92
Pronamide	19.61[a]	173	175, 145
Pyrene	24.02	202	200, 203
Terphenyl-d_{14} (surr.)	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	13.62[a]	216	214, 218
2,3,4,6-Tetrachlorophenol	16.09[a]	232	230, 131
2,4,6-Tribromophenol (surr.)	--	330	332, 141
1,2,4-Trichlorobenzene	9.67	180	182, 145
2,4,5-Trichlorophenol	13.00	196	198, 200
2,4,6-Trichlorophenol	12.85	196	198, 200
Toxaphene	--	159	231, 233

I.S. = internal standard
surr. = surrogate

[a]Estimated retention times.

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS**

Semivolatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
Phenol	108-95-2	10	660
bis(2-Chloroethyl) ether	111-44-4	10	660
2-Chlorophenol	95-57-8	10	660
1,3-Dichlorobenzene	541-73-1	10	660
1,4-Dichlorobenzene	106-46-7	10	660
Benzyl Alcohol	100-51-6	20	1300
1,2-Dichlorobenzene	95-50-1	10	660
2-Methylphenol	95-48-7	10	660
bis(2-Chloroisopropyl) ether	39638-32-9	10	660
4-Methylphenol	106-44-5	10	660
N-Nitroso-Di-N-propylamine	621-64-7	10	660
Hexachloroethane	67-72-1	10	660
Nitrobenzene	98-95-3	10	660
Isophorone	78-59-1	10	660
2-Nitrophenol	88-75-5	10	660
2,4-Dimethylphenol	105-67-9	10	660
Benzoic Acid	65-85-0	50	3300
bis(2-Chloroethoxy) methane	111-91-1	10	660
2,4-Dichlorophenol	120-83-2	10	660
1,2,4-Trichlorobenzene	120-82-1	10	660
Naphthalene	91-20-3	10	660
4-Chloroaniline	106-47-8	20	1300
Hexachlorobutadiene	87-68-3	10	660
4-Chloro-3-methylphenol	59-50-7	20	1300
2-Methylnaphthalene	91-57-6	10	660
Hexachlorocyclopentadiene	77-47-4	10	660
2,4,6-Trichlorophenol	88-06-2	10	660
2,4,5-Trichlorophenol	95-95-4	10	660

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS** (Continued)

Semivolatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
2-Chloronaphthalene	91-58-7	10	660
2-Nitroaniline	88-74-4	50	3300
Dimethyl phthalate	131-11-3	10	660
Acenaphthylene	208-96-8	10	660
3-Nitroaniline	99-09-2	50	3300
Acenaphthene	83-32-9	10	660
2,4-Dinitrophenol	51-28-5	50	3300
4-Nitrophenol	100-02-7	50	3300
Dibenzofuran	132-64-9	10	660
2,4-Dinitrotoluene	121-14-2	10	660
2,6-Dinitrotoluene	606-20-2	10	660
Diethylphthalate	84-66-2	10	660
4-Chlorophenyl phenyl ether	7005-72-3	10	660
Fluorene	86-73-7	10	660
4-Nitroaniline	100-01-6	50	3300
4,6-Dinitro-2-methylphenol	534-52-1	50	3300
N-Nitrosodiphenylamine	86-30-6	10	660
4-Bromophenyl phenyl ether	101-55-3	10	660
Hexachlorobenzene	118-74-1	10	660
Pentachlorophenol	87-86-5	50	3300
Phenanthrene	85-01-8	10	660
Anthracene	120-12-7	10	660
Di-n-butylphthalate	84-74-2	10	660
Fluoranthene	206-44-0	10	660
Pyrene	129-00-0	10	660
Butyl benzyl phthalate	85-68-7	10	660
3,3'-Dichlorobenzidine	91-94-1	20	1300
Benzo(a)anthracene	56-55-3	10	660
bis(2-ethylhexyl)phthalate	117-81-7	10	660

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TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS** (Continued)

Semi-Volatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
Chrysene	218-01-9	10	660
Di-n-octyl phthalate	117-84-0	10	660
Benzo(b)fluoranthene	205-99-2	10	660
Benzo(k)fluoranthene	207-08-9	10	660
Benzo(a)pyrene	50-32-8	10	660
Indeno(1,2,3-cd)pyrene	193-39-5	10	660
Dibenz(a,h)anthracene	53-70-3	10	660
Benzo(g,h,i)perylene	191-24-2	10	660

*PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis, therefore, PQLs will be higher based on the % moisture in each sample. This is based on a 30-g sample and gel permeation chromatography cleanup.

**Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable.

Other Matrices	Factor[1]
Medium-level soil and sludges by sonicator	7.5
Non-water-miscible waste	75

[1]PQL = [PQL for Ground Water (Table 2)] X [Factor].

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system:

4.1.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column: 30-m x 0.25-mm I.D. (or 0.32-mm I.D.) 1-um film thickness silicon-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer: Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 uL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

4.1.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry", Analytical Chemistry, 47, 995 (1975).

software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe: 10-uL.

5.0 REAGENTS

5.1 Stock standard solutions (1.00 ug/uL): Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.1.3 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

5.2 Internal standard solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Paragraph 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/uL. Each 1-mL sample extract undergoing analysis should be spiked with 10 uL of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard. Store at 4°C or less when not being used.

5.3 GC/MS tuning standard: A methylene chloride solution containing 50 ng/uL of decafluorotriphenylphosphine (DFTPP) should be prepared. The

standard should also contain 50 ng/uL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). Each 1-mL aliquot of calibration standard should be spiked with 10 uL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.5 Surrogate standards: The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.6 Matrix spike standards: See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation: Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.1.1 Direct injection: In very limited applications direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted where concentrations in excess of 10,000 ug/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorous pesticides	3620, 3640
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration: The recommended GC/MS operating conditions:

Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40°C for 4 min
Column temperature program: 40-270°C at 10°C/min
Final column temperature hold: 270°C (until benzo[g,h,i]perylene has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 uL
Carrier gas: Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

7.3.2 The internal standards selected in Paragraph 5.1 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion, i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation.

7.3.3 Analyze 1 uL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_x = Concentration of the compound being measured (ng/uL).

C_{is} = Concentration of the specific internal standard (ng/uL).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = 100[SD/$\overline{RF}$]) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.5 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average $\overline{RF}$ for these compounds SPCCs is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

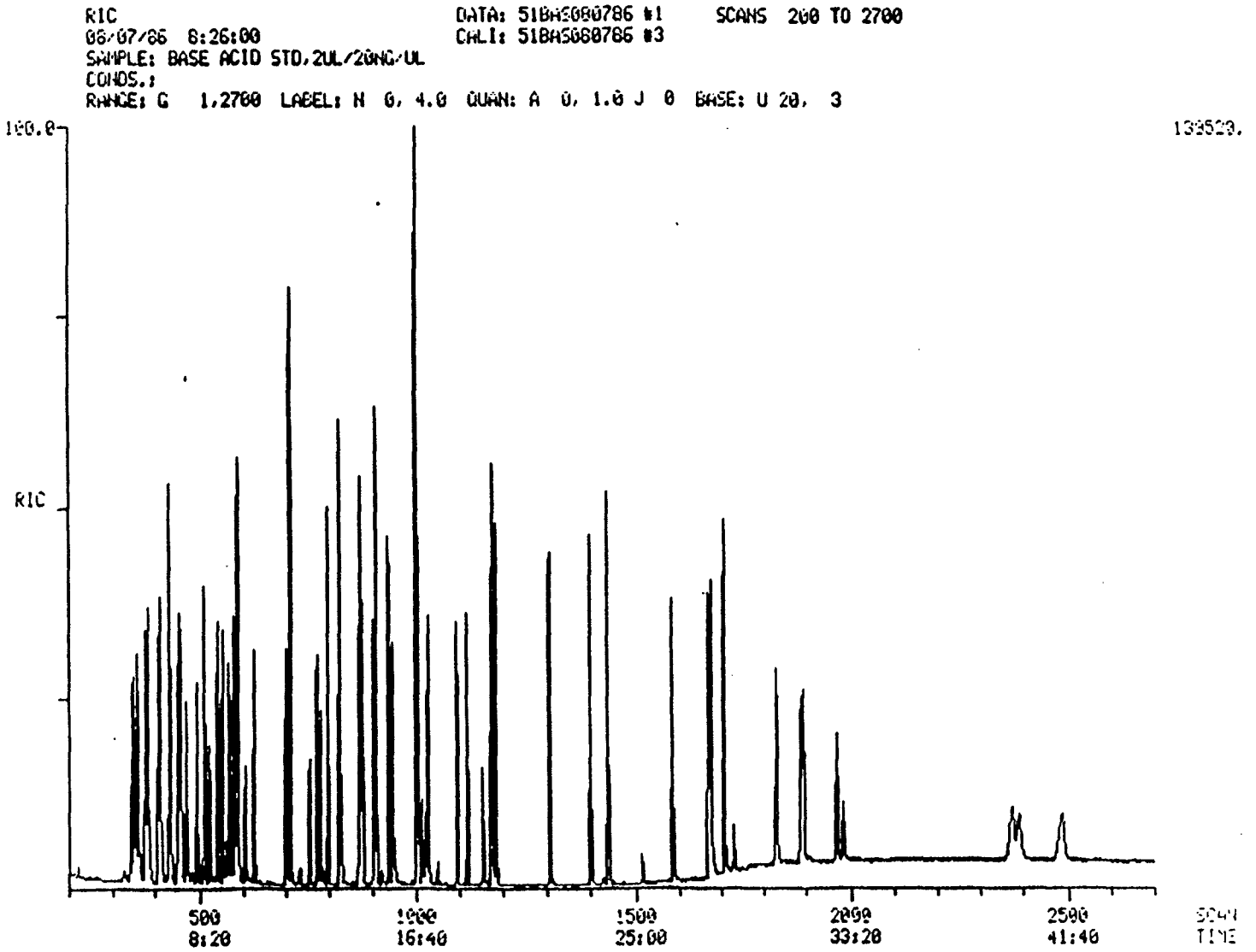

Figure 1. Gas chromatogram of base/neutral and acid calibration standard.

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TABLE 4. CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

7.4 Daily GC/MS calibration:

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12-hr shift.

7.4.2 A calibration standard(s) at mid-level concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12-hr during analysis. Compare the response factor data from the standards every 12-hr with the average response factor from the initial calibration for a specific instrument as per the SPCC (Paragraph 7.4.3) and CCC (Paragraph 7.4.4) criteria.

7.4.3 **System Performance Check Compounds (SPCCs):** A system performance check must be made during every 12 hr shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 **Calibration Check Compounds (CCCs):** After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_c}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_c = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.5 GC/MS analysis:

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1-mL extract obtained from sample preparation with 10 uL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1-mL extract by GC/MS using a 30-m x 0.25-mm (or 0.32-mm) silicone-coated fused-silica capillary column. The volume to be injected should ideally contain 100 ng of base/neutral and 200 ng of acid surrogates (for a 1 uL injection). The recommended GC/MS operating conditions to be used are specified in Paragraph 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Paragraph 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Data interpretation:

7.6.1 Qualitative analysis:

7.6.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

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7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Paragraph 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.6.2 Quantitative analysis:

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

V_t = Volume of total extract, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean V_t = 10,000 uL. If half the base/neutral extract and half the acid extract are combined, V_t = 2,000.

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.3.3).

V_o = Volume of water extracted (mL).

V_i = Volume of extract injected (uL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, RF, V_i = same as for water.

W_s = weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, or 1 for a wet-weight basis.

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr.)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr.) = surrogate

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz-(a)anthracene
Fluoranthene	Pyrene	Di-n-octylphthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7.6.2.5 Quantitation of multicomponent compounds (e.g., Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following sections:

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Section 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.3.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.4.3 and the CCC criteria in 7.4.4, each 12 hr.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 100 ug/mL in acetone. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Using a pipet, prepare QC check samples at a concentration of 100 ug/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.5.3 Analyze the well-mixed QC check samples according to the method beginning in Section 7.1 with extraction of the samples.

8.5.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte of interest using the four results.

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.5.2.

TABLE 6. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113

TABLE 6. QC ACCEPTANCE CRITERIA[a] - Continued

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike duplicate/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 ug/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte:

(1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100x'/T) $\pm$ 2.44(100S'/T)%.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Section 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC check standard by adding 1.0 mL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.96C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.06	0.26X-0.54
Aldrin	0.78C+1.66	0.27X-1.28	0.43X+1.13
Anthracene	0.80C+0.68	0.21X-0.32	0.27X-0.64
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22X+0.43	0.29X+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X+1.03	0.35X+0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18X+0.94	0.53X+0.92
β-BHC	0.87C-0.94	0.20X-0.58	0.30X+1.94
δ-BHC	0.29C-1.09	0.34X+0.86	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.99	0.35X+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X+1.34	0.26X+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X+0.28	0.25X+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X+0.73	0.36X+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X+0.66	0.16X+0.66
2-Chloronaphthalene	0.89C+0.01	0.07X+0.52	0.13X+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20X-0.94	0.30X-0.46
Chrysene	0.93C-1.00	0.28X+0.13	0.33X-0.09
4,4'-DDD	0.56C-0.40	0.29X-0.32	0.66X-0.96
4,4'-DDE	0.70C-0.54	0.26X-1.17	0.39X-1.04
4,4'-DDT	0.79C-3.28	0.42X+0.19	0.65X-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30X+8.51	0.59X+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13X+1.16	0.39X+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20X+0.47	0.24X+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25X+0.68	0.41X+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X+0.23	0.29X+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28X+7.33	0.47X+3.45
Dieldrin	0.82C-0.16	0.20X-0.16	0.26X-0.07
Diethyl phthalate	0.43C+1.00	0.28X+1.44	0.52X+0.22
Dimethyl phthalate	0.20C+1.03	0.54X+0.19	1.05X-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12X+1.06	0.21X+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14X+1.26	0.19X+0.35
Di-n-octylphthalate	0.76C-0.79	0.21X+1.19	0.37X+1.19
Endosulfan sulfate	0.39C+0.41	0.12X+2.47	0.63X-1.03
Endrin aldehyde	0.76C-3.86	0.18X+3.91	0.73X-0.62
Fluoranthene	0.81C+1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X+0.26	0.13X+0.61
Heptachlor	0.87C-2.97	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.33X-0.46	0.28X+0.64
Hexachlorobenzene	0.74C+0.66	0.18X-0.10	0.43X-0.52
Hexachlorobutadiene	0.71C-1.01	0.19X+0.92	0.26X+0.49
Hexachloroethane	0.73C-0.83	0.17X+0.67	0.17X+0.80

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a] - Continued

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{X}$+1.46	0.50$\bar{X}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{X}$+0.77	0.33$\bar{X}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{X}$-0.41	0.30$\bar{X}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{X}$+0.92	0.27$\bar{X}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{X}$+0.68	0.44$\bar{X}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{X}$+3.61	0.43$\bar{X}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{X}$+0.57	0.15$\bar{X}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{X}$+0.06	0.15$\bar{X}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{X}$+0.85	0.21$\bar{X}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{X}$+0.75	0.29$\bar{X}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{X}$+1.46	0.28$\bar{X}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{X}$+1.25	0.21$\bar{X}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{X}$+1.21	0.22$\bar{X}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{X}$+2.36	0.42$\bar{X}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{X}$+42.29	0.26$\bar{X}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{X}$+2.57	0.44$\bar{X}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{X}$+3.03	0.30$\bar{X}$+4.33
Phenol	0.43C+1.26	0.26$\bar{X}$+0.73	0.35$\bar{X}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{X}$+2.22	0.22$\bar{X}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

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9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 ug/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

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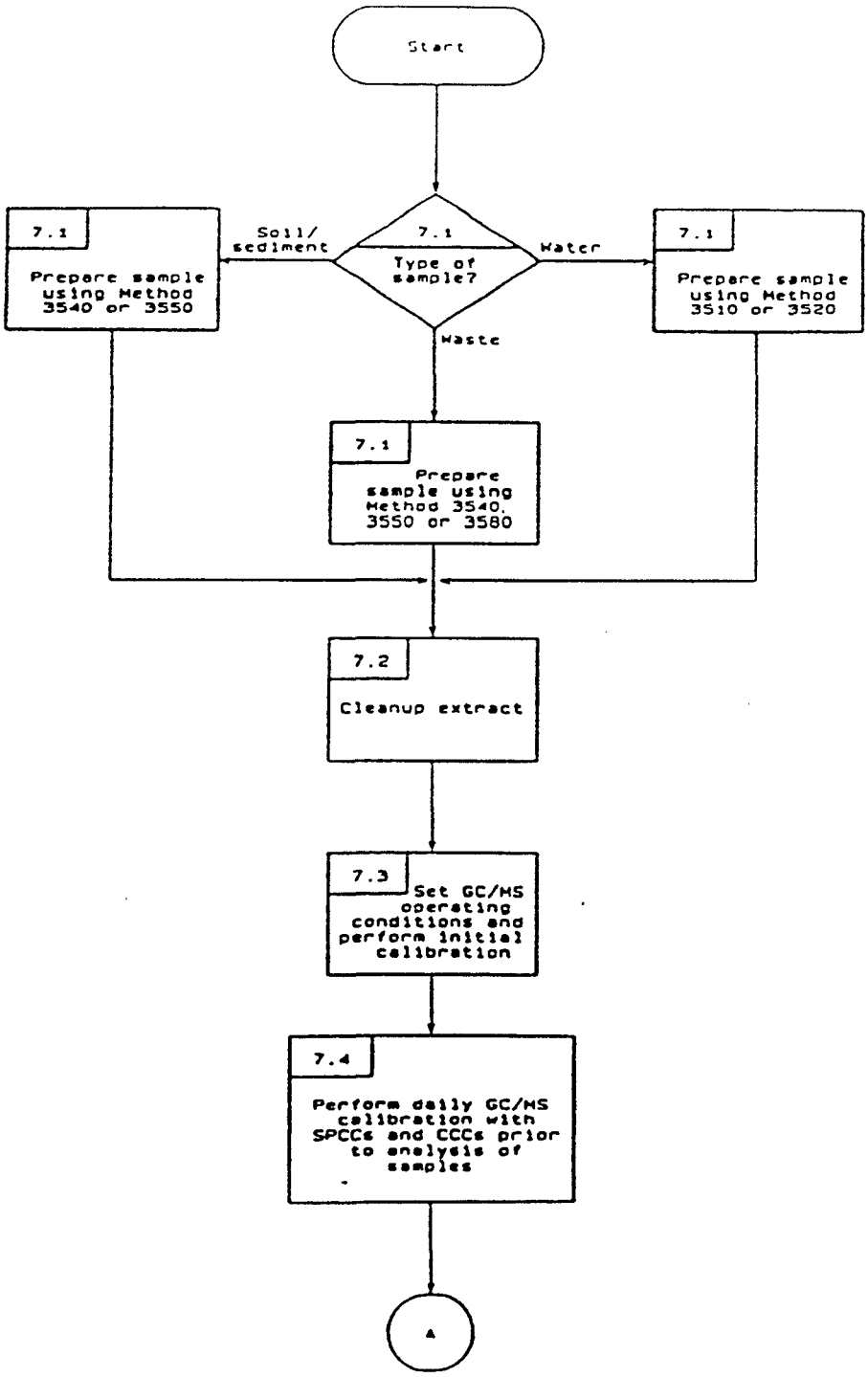
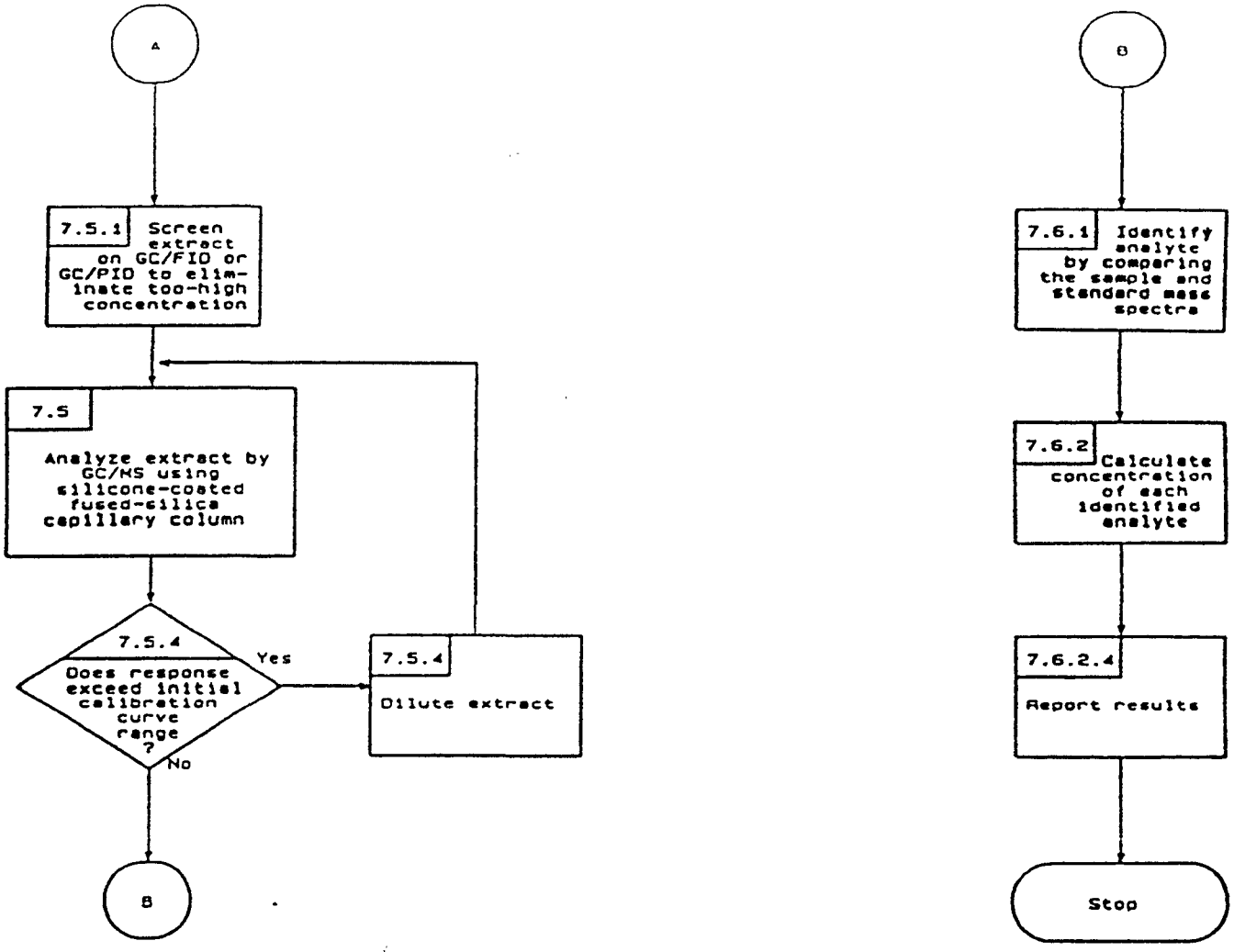

Start
7.1
Type of sample?
Soil/ sediment
Water
Waste
7.1
Prepare sample using Method 3540 or 3550
7.1
Prepare sample using Method 3510 or 3520
7.1
Prepare sample using Method 3540, 3550 or 3580
7.2
Cleanup extract
7.3
Set GC/MS operating conditions and perform initial calibration
7.4
Perform daily GC/MS calibration with SPCCs and CCCs prior to analysis of samples
A


A
7.5.1 Screen extract on GC/FID or GC/PID to eliminate too-high concentration
7.5 Analyze extract by GC/MS using silicone-coated fused-silica capillary column
7.5.4 Does response exceed initial calibration curve range ?
Yes
7.5.4 Dilute extract
No
B
B
7.6.1 Identify analyte by comparing the sample and standard mass spectra
7.6.2 Calculate concentration of each identified analyte
7.6.2.4 Report results
Stop

METHOD 9045

SOIL pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure which has been approved for measuring pH in calcareous and noncalcareous soils.

2.0 SUMMARY OF METHOD

2.1 The soil sample is mixed either with Type II water or with a calcium chloride solution (see Section 5.0), depending on whether the soil is considered calcareous or noncalcareous. The pH of the solution is then measured with a pH meter.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can either (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Electrodes:

4.2.1 Calomel electrode.

4.2.2 Glass electrode.

4.2.3 A combination electrode can be employed instead of calomel or glass.

4.5 Beaker: 50-mL.

4.6 Volumetric flask: 2-Liter.

4.7 Volumetric flask: 1-Liter.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Primary standard buffer salts are available from the National Bureau of Standards (NBS) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NBS salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NBS standards, are recommended for routine use.

5.4 Stock calcium chloride solution ($CaCl_2$), 3.6 M: Dissolve 1059 g of $CaCl_2 \cdot 2H_2O$ in Type II water in a 2-liter volumetric flask. Cool the solution, dilute it to volume with Type II water, and mix it well. Dilute 20 mL of this solution to 1 liter with Type II water in a volumetric flask and standardize it by titrating a 25-mL aliquot of the diluted solution with standard 0.1 N $AgNO_3$, using 1 mL of 5% K_2CrO_4 as the indicator.

5.5 Calcium chloride ($CaCl_2$), 0.01 M: Dilute 50 mL of stock 3.6 M $CaCl_2$ to 18 liters with Type II water. If the pH of this solution is not between 5 and 6.5, adjust the pH by adding a little $Ca(OH)_2$ or HCl. As a check on the preparation of this solution, measure its electrical conductivity. The specific conductivity should be 2.32 $\pm$ 0.08 mmho per cm at 25°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Sample preparation and pH measurement of noncalcareous soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of Type II water and stir the suspension several times during the next 30 min.

7.2.2 Let the soil suspension stand for about 1 hr to allow most of the suspended clay to settle out from the suspension.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.5 Report the results as "soil pH measured in water."

7.3 Sample preparation and pH measurement of calcareous soils:

7.3.1 To 10 g of soil in a 50-mL beaker, add 20 mL of 0.01 M $CaCl_2$ (Step 5.5) solution and stir the suspension several times during the next 30 min.

7.3.2 Let the soil suspension stand for about 30 min to allow most of the suspended clay to settle out from the suspension.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed well into the partly settled suspension and the calomel electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "soil pH measured in 0.01 M $CaCl_2$".

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8.0 QUALITY CONTROL

8.1 Duplicate samples and check standards should be analyzed routinely.

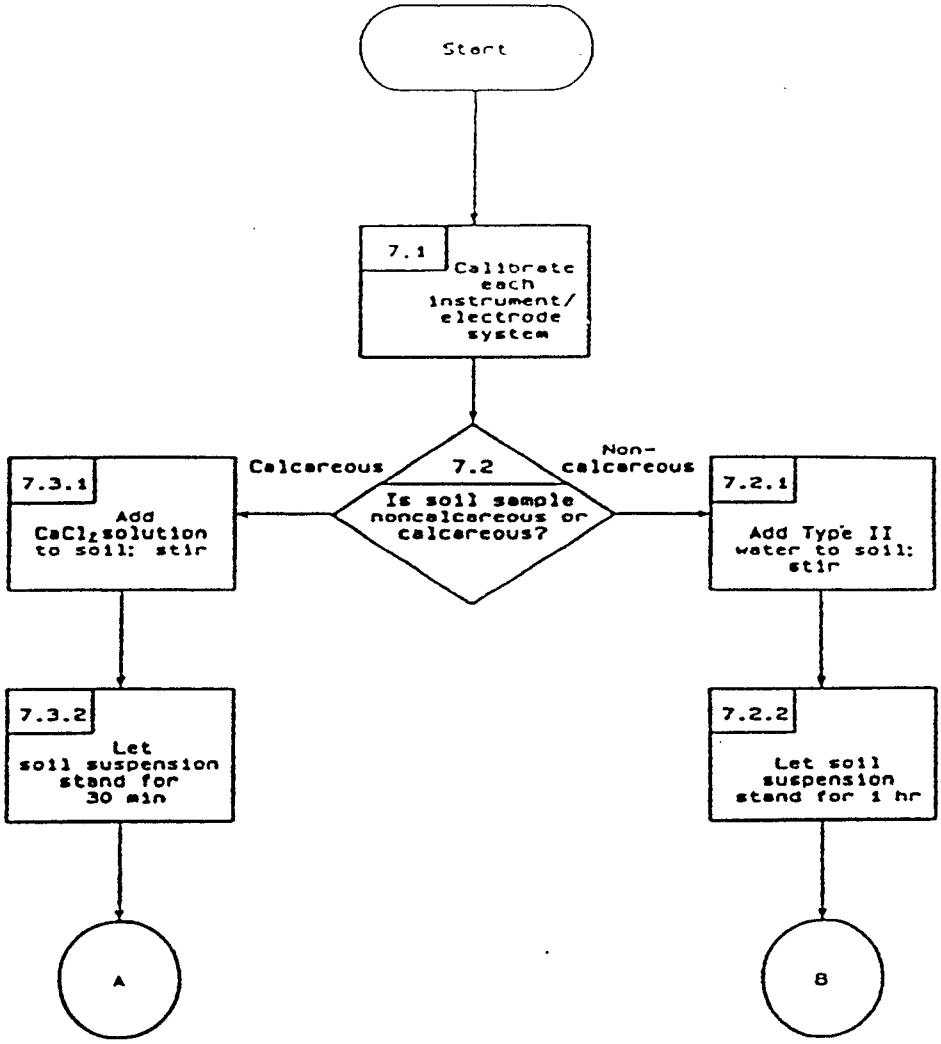
8.2 Electrodes must be thoroughly rinsed between samples.

9.0 METHOD PERFORMANCE

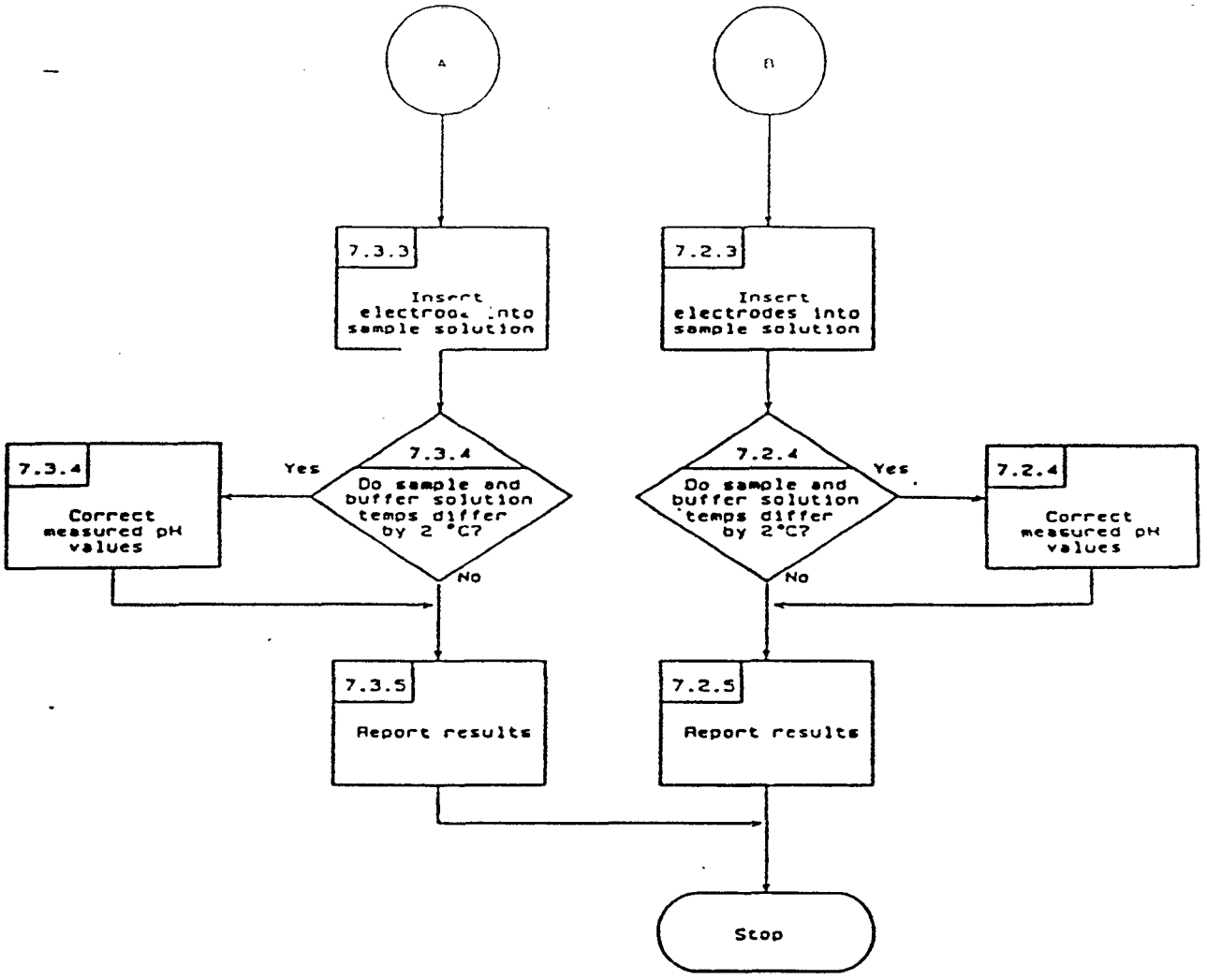
9.1 No data provided.

10.0 REFERENCES

10.1 None required.


Start
7.1
Calibrate each instrument/ electrode system
7.2
Is soil sample noncalcareous or calcareous?
Calcareous
Non-calcareous
7.3.1
Add $CaCl_2$ solution to soil: stir
7.2.1
Add Type II water to soil: stir
7.3.2
Let soil suspension stand for 30 min
7.2.2
Let soil suspension stand for 1 hr
A
B

300705


A
B
7.3.3
Insert electrodes into sample solution
7.2.3
Insert electrodes into sample solution
7.3.4
Do sample and buffer solution temps differ by 2 °C?
Yes
No
7.3.4
Correct measured pH values
7.2.4
Do sample and buffer solution temps differ by 2°C?
Yes
No
7.2.4
Correct measured pH values
7.3.5
Report results
7.2.5
Report results
Stop

300706

METHOD 9050

SPECIFIC CONDUCTANCE

1.0 SCOPE AND APPLICATION

1.1 Method 9050 is used to measure the specific conductance of drinking, ground, surface, and saline waters and domestic and industrial aqueous wastes. Method 9050 is not applicable to solid samples.

2.0 SUMMARY OF METHOD

2.1 The specific conductance of a sample is measured using a self-contained conductivity meter (Wheatstone bridge-type or equivalent).

2.2 Whenever possible, samples are analyzed at 25°C. If samples are analyzed at different temperatures, temperature corrections must be made and results reported at 25°C.

3.0 INTERFERENCES

3.1 Platinum electrodes can degrade and cause erratic results. When this happens, as evidenced by erratic results or flaking off of the platinum black, the electrode should be replatinized.

3.2 The specific conductance cell can become coated with oil and other materials. It is essential that the cell be thoroughly rinsed and, if necessary, cleaned between samples.

4.0 APPARATUS AND MATERIALS

4.1 Self-contained conductivity instruments: an instrument consisting of a source of alternating current, a Wheatstone bridge, null indicator, and a conductivity cell or other instrument measuring the ratio of alternating current through the cell to voltage across it. The latter has the advantage of a linear reading of conductivity. Choose an instrument capable of measuring conductivity with an error not exceeding 1% or 1 umho/cm, whichever is greater.

4.2 Platinum-electrode or non-platinum-electrode specific conductance cell.

4.3 Water bath.

4.4 Thermometer: capable of being read to the nearest 0.1°C and covering the range 23° to 27°C. An electrical thermometer having a small thermistor sensing element is convenient because of its rapid response.

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5.0 REAGENTS

5.1 Conductivity water: Pass distilled water through a mixed-bed deionizer and discard first 1,000 mL. Conductivity should be less than 1 umho/cm.

5.2 Standard potassium chloride (0.0100 M): Dissolve 0.7456 g anhydrous KCl in conductivity water and make up to 1,000 mL at 25°C. This solution will have a specific conductance of 1,413 umho/cm at 25°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed and thoroughly rinsed. Both plastic and glass containers are suitable.

6.3 Aqueous samples should be stored at 4°C and analyzed within 24-hr.

7.0 PROCEDURE

7.1 Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01 N KCl solution. Adjust temperature of a fourth portion to 25.0 ± 0.1°C. Measure resistance of this portion and note temperature. Compute cell constant, C:

$$C = (0.001413)(R_{KCl})\ 1 + 0.0191\ (t - 25)$$

where:

R_{KCl} = measured resistance, ohms; and

t = observed temperature, °C.

7.2 Conductivity measurement: Rinse cell with one or more portions of sample. Adjust temperature of a final portion to 25.0 ± 0.1°C. Measure sample resistance or conductivity and note temperature.

7.3 Calculation: The temperature coefficient of most waters is only approximately the same as that of standard KCl solution; the more the temperature of measurement deviates from 25.0°C, the greater the uncertainty in applying the temperature correction. Report all conductivities at 25.0°C.

300708

7.3.1 When sample resistance is measured, conductivity at 25°C is:

$$K = \frac{(1{,}000{,}000)(C)}{R_m \quad 1 + 0.0191\ (t - 25)}$$

where:

K = conductivity, umho/cm;
C = cell constant, cm-L;
R_m = measured resistance of sample, ohms; and
t = temperature of measurement.

7.3.2 When sample conductivity is measured, conductivity at 25°C is:

$$K = \frac{(K_m)(1{,}000{,}000)(C)}{1 + 0.0191\ (t - 25)}$$

where:

K_m = measured conductivity, umho at t°C, and other units are defined as above.

NOTE: If conductivity readout is in umho/cm, delete the factor 1,000,000 in the numerator.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Analyze check standards after approximately every 15 samples.

8.3 Run 1 duplicate sample for every 10 samples.

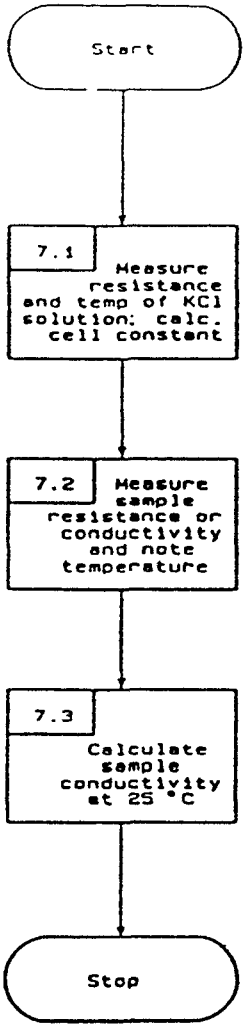
9.0 METHOD PERFORMANCE

9.1 Three synthetic samples were tested with the following results:

Conductivity umhos/cm	No. of Results	Relative Standard Deviation %	Relative Error %
147.0	117	8.6	9.4
303.0	120	7.8	1.9
228.0	120	8.4	3.0

10.0 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 16th ed. (1985), Method 205.



300711

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METHOD 9060

TOTAL ORGANIC CARBON

1.0 SCOPE AND APPLICATION

1.1 Method 9060 is used to determine the concentration of organic carbon in ground water, surface and saline waters, and domestic and industrial wastes. Some restrictions are noted in Sections 2.0 and 3.0.

1.2 Method 9060 is most applicable to measurement of organic carbon above 1 mg/L.

2.0 SUMMARY OF METHOD

2.1 Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by either catalytic combustion or wet chemical oxidation. The CO_2 formed is then either measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

2.2 Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, the manner of preliminary sample treatment as well as the instrument settings will determine which forms of carbon are actually measured. The forms of carbon that can be measured by Method 9060 are:

1. Soluble, nonvolatile organic carbon: e.g., natural sugars.
2. Soluble, volatile organic carbon: e.g., mercaptans, alkanes, low molecular weight alcohols.
3. Insoluble, partially volatile carbon: e.g., low molecular weight oils.
4. Insoluble, particulate carbonaceous materials: e.g., cellulose fibers.
5. Soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter: e.g., oily matter adsorbed on silt particles.

2.3 Carbonate and bicarbonate are inorganic forms of carbon and must be separated from the total organic carbon value. Depending on the instrument manufacturer's instructions, this separation can be accomplished by either a simple mathematical subtraction, or by removing the carbonate and bicarbonate by converting them to CO_2 with degassing prior to analysis.

300712

3.0 INTERFERENCES

3.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter-type syringe or pipet. The openings of the syringe or pipet limit the maximum size of particle which may be included in the sample.

3.3 Removal of carbonate and bicarbonate by acidification and purging with nitrogen, or other inert gas, can result in the loss of volatile organic substances.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

4.2 Apparatus for total and dissolved organic carbon:

4.2.1 Several companies manufacture analyzers for measuring carbonaceous material in liquid samples. The most appropriate system should be selected based on consideration of the types of samples to be analyzed, the expected concentration range, and the forms of carbon to be measured.

4.2.2 No specific analyzer is recommended as superior. If the technique of chemical oxidation is used, the laboratory must be certain that the instrument is capable of achieving good carbon recoveries in samples containing particulates.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities, and should be boiled and cooled to remove CO_2.

5.2 Potassium hydrogen phthalate, stock solution, 1,000 mg/L carbon: Dissolve 0.2128 g of potassium hydrogen phthalate (primary standard grade) in Type II water and dilute to 100.0 mL.

NOTE: Sodium oxalate and acetic acid are not recommended as stock solutions.

5.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with Type II water.

5.4 Carbonate-bicarbonate, stock solution, 1,000 mg/L carbon: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100-mL volumetric flask. Dissolve with Type II water.

5.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to Step 5.3.

NOTE: This standard is not required by some instruments.

5.6 Blank solution: Use the same Type II water as was used to prepare the standard solutions.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

NOTE: A brief study performed in the EPA Laboratory indicated that Type II water stored in new, 1-qt cubitainers did not show any increase in organic carbon after 2 weeks' exposure.

6.3 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between sample collection and the start of analysis should be minimized. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

6.4 In instances where analysis cannot be performed within 2 hr from time of sampling, the sample is acidified (pH $\leq$ 2) with HCl or H_2SO_4.

7.0 PROCEDURE

7.1 Homogenize the sample in a blender.

NOTE: To avoid erroneously high results, inorganic carbon must be accounted for. The preferred method is to measure total carbon and inorganic carbon and to obtain the organic carbon by subtraction. If this is not possible, follow Steps 7.2 and 7.3 prior to analysis; however, volatile organic carbon may be lost.

7.2 Lower the pH of the sample to 2.

7.3 Purge the sample with nitrogen for 10 min.

7.4 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

7.5 For calibration of the instrument, a series of standards should be used that encompasses the expected concentration range of the samples.

7.6 Quadruplicate analysis is required. Report both the average and the range.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Verify calibration with an independently prepared check standard every 15 samples.

8.4 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

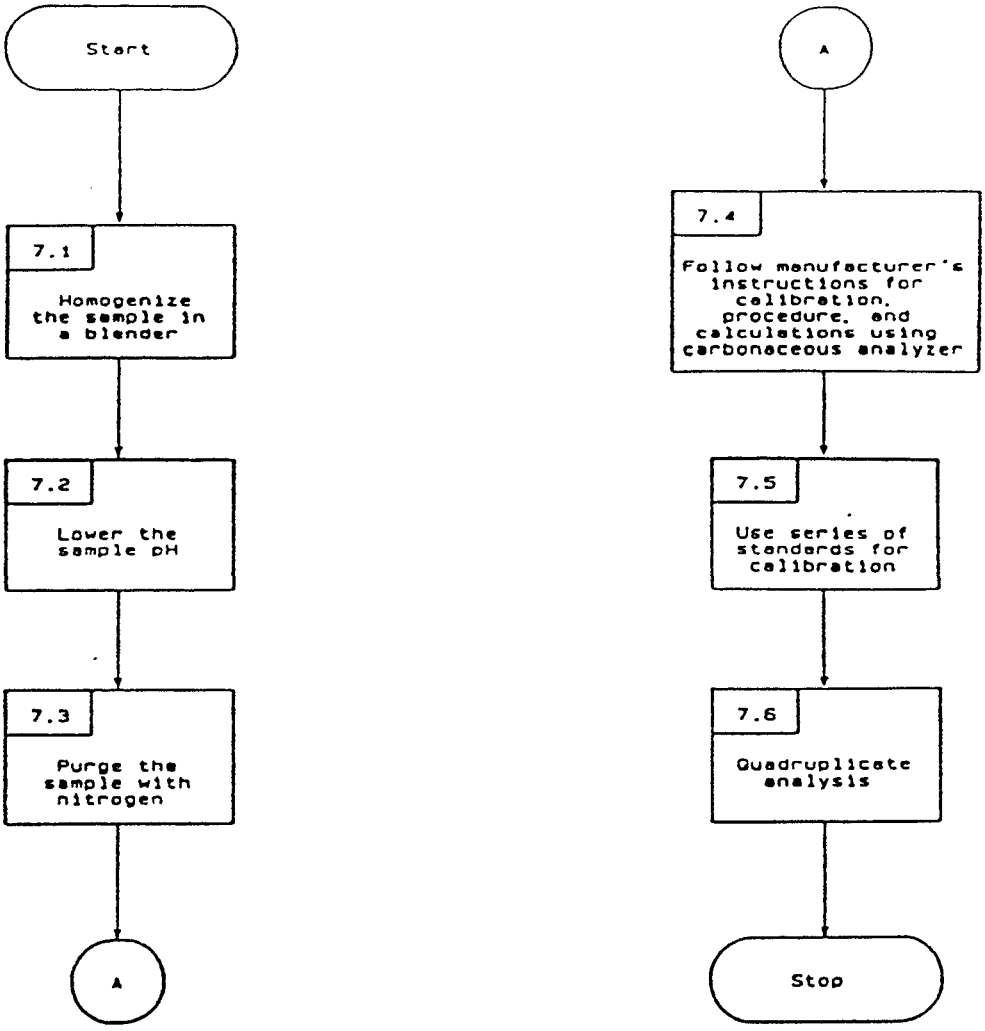
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 415.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976).

2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 532, Method 505 (1975).


Start
7.1
Homogenize the sample in a blender
7.2
Lower the sample pH
7.3
Purge the sample with nitrogen
A
A
7.4
Follow manufacturer's instructions for calibration, procedure, and calculations using carbonaceous analyzer
7.5
Use series of standards for calibration
7.6
Quadruplicate analysis
Stop

300716

METHOD 9080

CATION-EXCHANGE CAPACITY OF SOILS (AMMONIUM ACETATE)

1.0 SCOPE AND APPLICATION

1.1 Method 9080 is used to determine the cation-exchange capacity of soils. The method is not applicable to soils containing appreciable amounts of vermiculite clays, kaolin, halloysite, or other 1:1-type clay minerals. They should be analyzed by the sodium acetate method (Method 9081). That method (9081) is also generally the preferred method for very calcareous soils. For distinctly acid soils, the cation-exchange capacity by summation method (Chapman, p. 900; see Paragraph 10.1) should be employed.

2.0 SUMMARY

2.1 The soil is mixed with an excess of 1 N ammonium acetate solution. This results in an exchange of the ammonium cations for exchangeable cations present in the soil. The excess ammonium is removed, and the amount of exchangeable ammonium is determined.

3.0 INTERFERENCES

3.1 Soils containing appreciable vermiculite clays, kaolin, halloysite, or other 1:1-type clay minerals will often give lower values for exchange capacity. See Paragraph 1.1 above.

3.2 With calcareous soils, the release of calcium carbonate from the soil into the ammonium acetate solution limits the saturation of exchange sites by the ammonium ion. This results in artificially low cation-exchange capacities.

4.0 APPARATUS AND MATERIALS

4.1 Erlenmeyer flask: 500-mL.

4.2 Buchner funnel or equivalent: 55-mm.

4.3 Sieve: 2-mm.

4.4 Aeration apparatus (assembled as in Figure 1):

4.4.1 Kjeldahl flask: 800-mL.

4.4.2 Erlenmeyer flask: 800-mL.

4.4.3 Glass wool filter.

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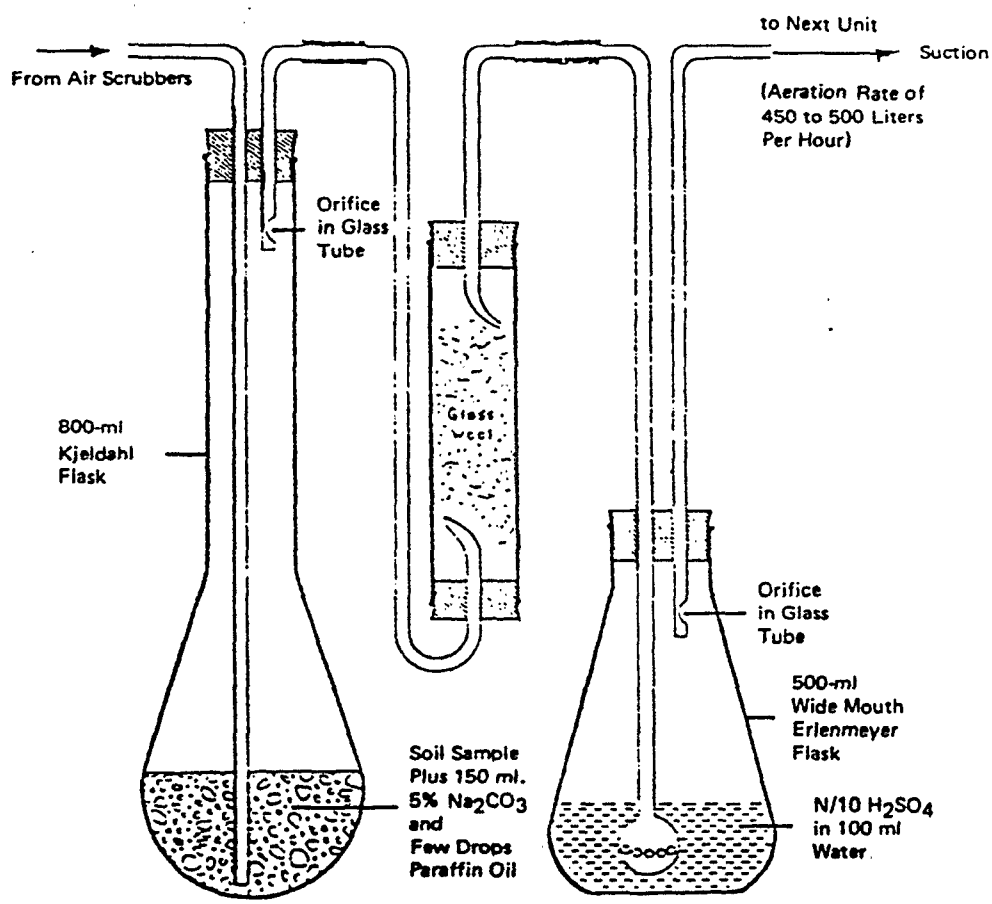

Figure 1. Diagram of aeration unit for determination of absorbed ammonia. Six to twelve such units is a convenient number for routine work; they can be mounted on a portable rack. (Apparatus as modified by Dr. A. P. Vanselow, Dept. of Soils & Plant Nutrition, Univerity of California, Riverside, Calif.).

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4.4.4 Glass tubing.

4.4.5 Flow meter.

5.0 REAGENTS

5.1 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 mL of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 mL of concentrated ammonium hydroxide (NH_4OH) and add water to obtain a volume of about 1,980 mL. Check the pH of the resulting solution, add more NH_4OH, as needed, to obtain a pH of 7, and dilute the solution to a volume of 2 liters with water.

5.2 Isopropyl alcohol: 99%.

5.3 Ammonium chloride (NH_4Cl), 1 N: Dissolve 53.49 g of NH_4Cl in Type II water, adjust the pH to 7.0 with NH_4OH, and dilute to 1 L.

5.4 Ammonium chloride (NH_4Cl), 0.25 N: Dissolve 13.37 g of NH_4Cl in Type II water, adjust the pH to 7.0 with NH_4OH, and dilute to 1 L.

5.5 Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$), 10%: Add 90 mL of Type II water to 10 g of ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) and mix well.

5.6 Dilute ammonium hydroxide (NH_4OH): Add 1 volume of concentrated NH_4OH to an equal volume of water.

5.7 Silver nitrate ($AgNO_3$), 0.10 N: Dissolve 15.39 g of $NgNO_3$ in Type II water, mix well, and dilute to 1 L.

5.8 Reagents for aeration option:

5.8.1 Sodium carbonate solution (Na_2CO_3), 5%: Add 95 mL of Type II water to 5 g of Na_2CO_3 and mix well.

5.8.2 Paraffin oil.

5.8.3 Sulfuric acid (H_2SO_4), 0.1 N standard: Add 2.8 mL concentrated H_2SO_4 to Type II water and dilute to 1 L. Standardize against a base of known concentration.

5.8.4 Sodium hydroxide (NaOH), 0.1 N standard: Dissolve 4.0 g NaOH in Type II water and dilute to 1 L. Standardize against an acid of known concentration.

5.8.5 Methyl red indicator, 0.1%: Dissolve 0.1 g in 99.9 mL of 95% ethanol and mix well.

5.9 Reagents for distillation option:

5.9.1 Sodium chloride, NaCl (acidified), 10%: Dissolve 100 g of NaCl (ammonium-free) in 900 mL of Type II water; mix well. Add approximately 0.42 mL of concentrated HCl to make the solution approximately 0.005 N.

5.9.2 Sodium hydroxide (NaOH), 1 N: Dissolve 40 g of NaOH in Type II water and dilute to 1 L.

5.9.3 Boric acid (H_3BO_3), 2% solution: Dissolve 20 g H_3BO_3 in 980 mL Type II water and mix well.

5.9.4 Standard sulfuric acid (H_2SO_4), 0.1 N: See Step 5.8.3.

5.9.5 Bromocresol green-methyl red mixed indicator: Triturate 0.1 g of bromocresol green with 2 mL 0.1 N NaOH in an agate mortar and add 95% ethyl alcohol to obtain a total volume of 100 mL. Triturate 0.1 g of methyl red with a few mL of 95% ethyl alcohol in an agate mortar. Add 3 mL of 0.1 N NaOH and dilute the solution to a volume of 100 mL with 95% ethyl alcohol. Mix 75 mL of the bromocresol green solution with 25 mL of the methyl red solution and dilute the mixture to 200 mL with 95% ethyl alcohol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Sieve a sample aliquot of the soil through a 2-mm screen and allow the sieved soil to air dry (at a temperature of $\leq$60°C). Place 10 g of the air-dried soil in a 500-mL Erlenmeyer flask and add 250 mL of neutral, 1 N NH_4OAc. (Use 25 g of soil if the exchange capacity is very low, e.g., 3-5 meq per 100 g.) Shake the flask thoroughly and allow it to stand overnight.

7.2 Filter the soil with light suction using a 55-mm Buchner funnel or equivalent. Do not allow the soil to become dry and cracked.

7.3 Leach the soil with the neutral NH_4OAc reagent until no test for calcium can be obtained in the effluent solution. (For the calcium test, add a few drops each of 1 N NH_4Cl and 10% ammonium oxalate, dilute NH_4OH to 10 mL of the leachate in a test tube, and heat the solution to near the boiling point. The presence of calcium is indicated by a white precipitate or turbidity.)

7.4 Then leach the soil four times with neutral 1 N NH_4Cl and once with 0.25 N NH_4Cl.

7.5 Wash out the electrolyte with 150 to 200 mL of 99% isopropyl alcohol. When the test for chloride in the leachate (use 0.10 $AgNO_3$) becomes negligible, allow the soil to drain thoroughly.

7.6 Determine the adsorbed NH_4 either by the aeration method (Paragraph 7.7) or by the acid-NaCl method (Paragraph 7.8).

7.7 Aeration method:

7.7.1 Place an excess of 0.1 N standard H_2SO_4 in the 500-mL Erlenmeyer flask on the aeration apparatus (50 mL is an ample quantity for most soils) and add 10 drops of methyl red indicator and enough distilled water to make the total volume about 100 mL.

7.7.2 Attach the flask to the apparatus. Then transfer the ammonium-saturated sample of soil (from Paragraph 7.5) quantitatively to the 800-mL Kjeldahl flask located in the flow line just before the Erlenmeyer flask with the standard acid. Use a rubber policeman and a stream of distilled water from a wash bottle, as needed, to complete the transfer.

7.7.3 Add 150 mL Na_2CO_3 solution and a few drops of paraffin oil and attach the flask to the apparatus.

7.7.4 Apply suction to the outflow end of the apparatus and adjust the rate of flow to 450 to 500 liters of air per hr. Continue the aeration for 17 hr.

7.7.5 Shut off the suction and remove the flask. Titrate the residual acid in the absorption solutions with standard 0.1 N NaOH from the original red color through orange to yellow at the end point. From the titration values obtained with the soil and blank solutions, calculate the content of adsorbed ammonium in milligram equivalents per 100 g soil.

7.8 Acid-NaCl method:

7.8.1 Leach the ammonium-saturated soil from Paragraph 7.5 with 10% acidified NaCl until 225 mL have passed through the sample. Add small portions at a time, allowing each portion to pass through the sample before adding the next portion.

7.8.2 Transfer the leachate quantitatively to an 800-mL Kjeldahl flask, add 25 mL of 1 N NaOH, and distill 60 mL of the solution into 50 mL of 2% H_3BO_3.

7.8.3 Add 10 drops of bromocresol green-methyl red mixed indicator and titrate the boric acid solution with standard 0.1 N H_2SO_4. The color change is from bluish green through bluish purple to pink at the end point. Run blanks on the reagents. Correct the titration figure for the blanks and calculate the milliequivalents of ammonium in 100 g of soil.

7.8.4 Results should be reported as "determined with ammonium acetate" at pH 7.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Material of known cation-exchange capacity must be routinely analyzed.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. This method is based on Chapman, H.D., "Cation-exchange Capacity," pp. 891-900, in C.A. Black (ed.), Method of Soil Analysis, Part 2: Chemical and Microbiological Properties, Am. Soc. Agron., Madison, Wisconsin (1965).

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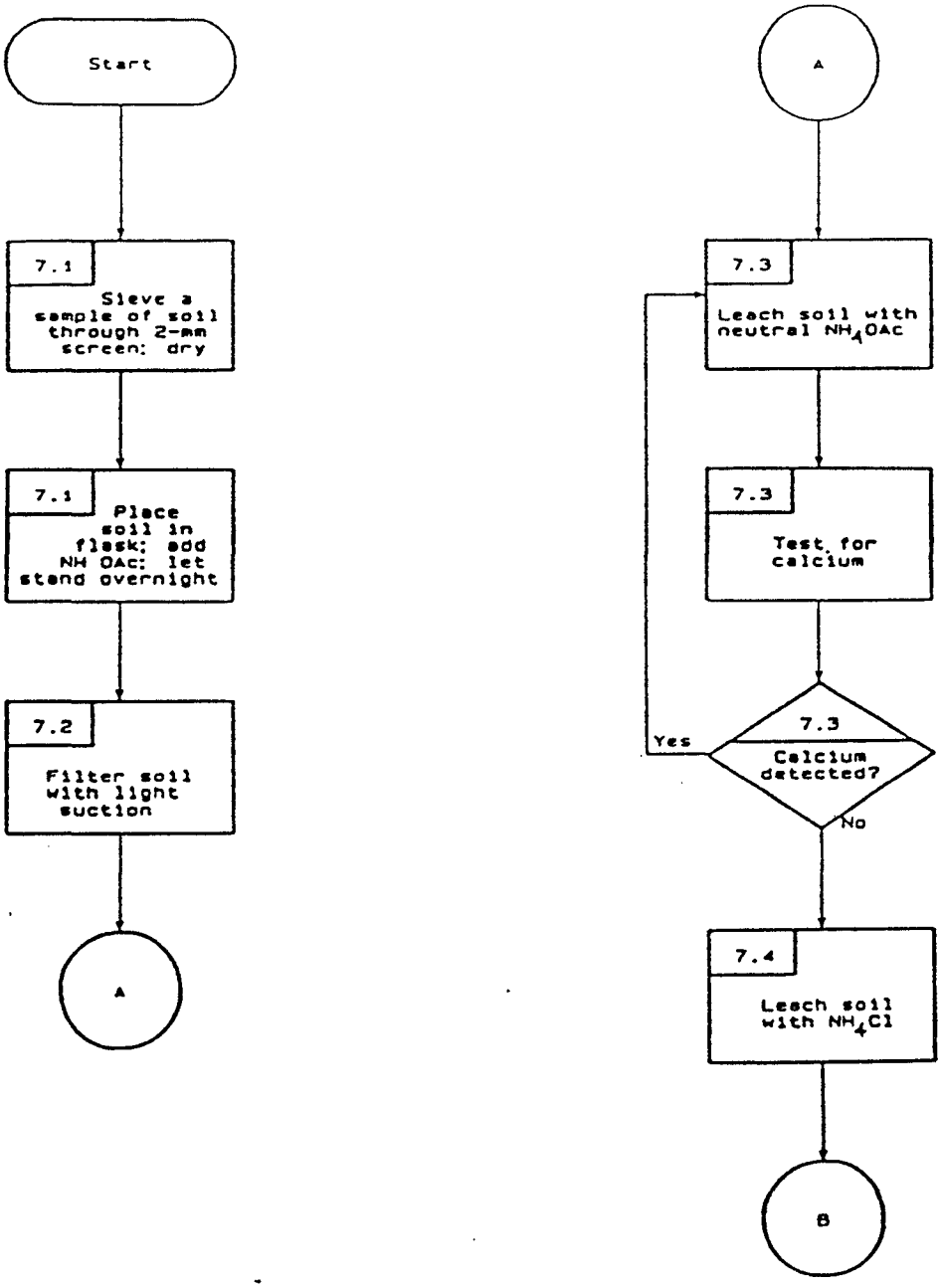
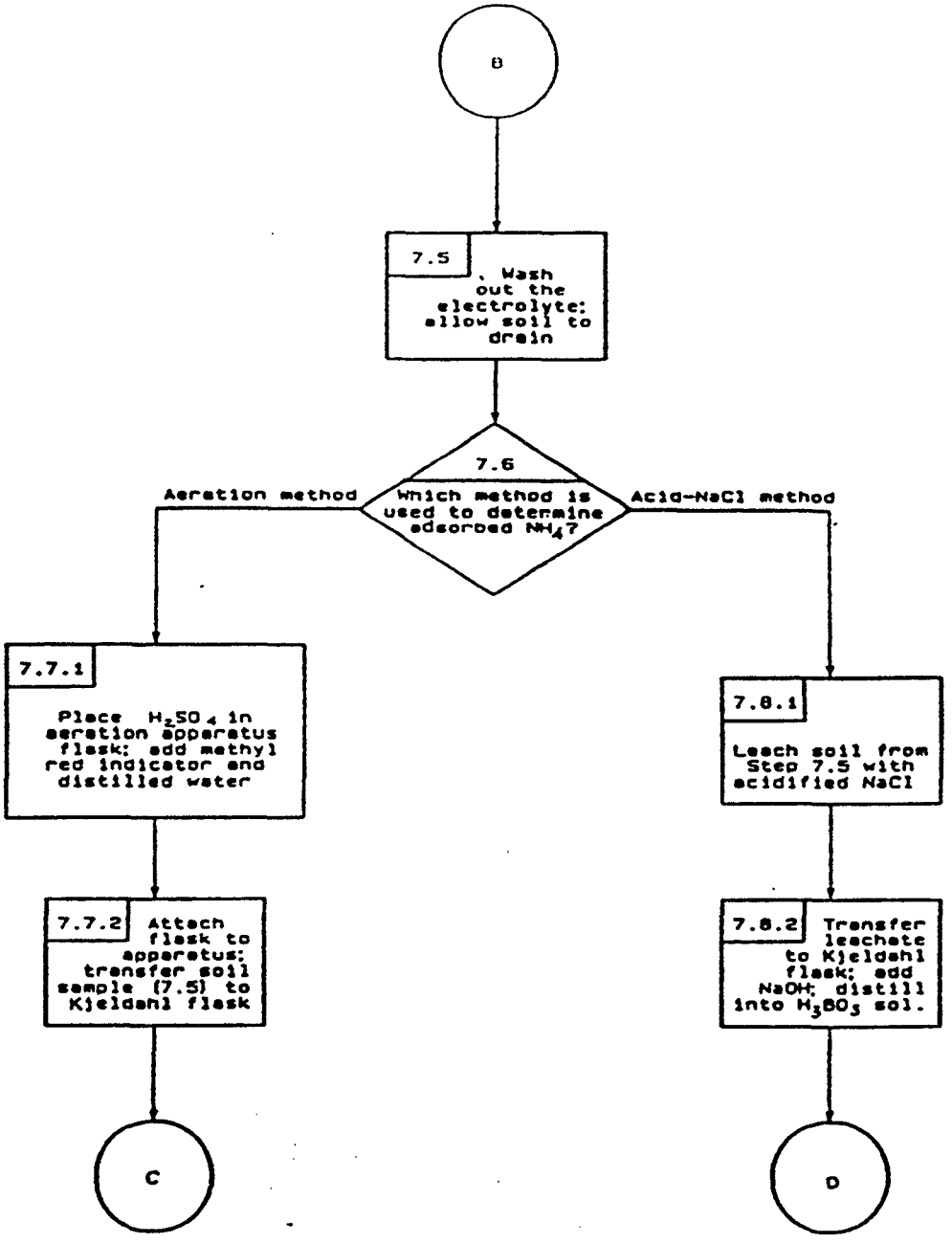
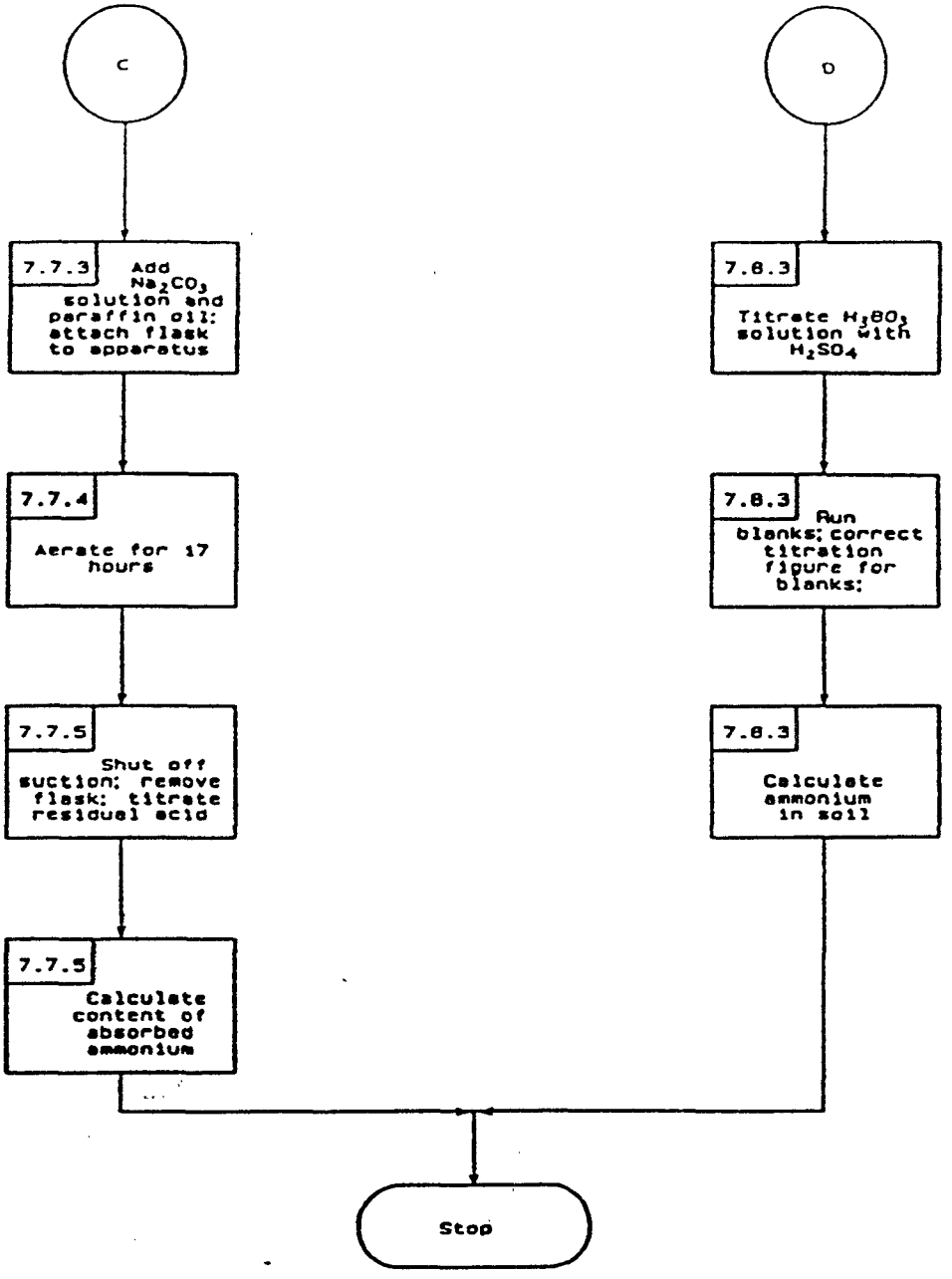

Start
7.1
Sieve a sample of soil through 2-mm screen; dry
7.1
Place soil in flask; add NH OAc; let stand overnight
7.2
Filter soil with light suction
A
A
7.3
Leach soil with neutral NH4OAc
7.3
Test for calcium
7.3
Calcium detected?
Yes
No
7.4
Leach soil with NH4Cl
B


B
7.5
. Wash out the electrolyte: allow soil to drain
7.6
Which method is used to determine adsorbed NH_4?
Aeration method
Acid-NaCl method
7.7.1
Place H_2SO_4 in aeration apparatus flask; add methyl red indicator and distilled water
7.7.2
Attach flask to apparatus; transfer soil sample (7.5) to Kjeldahl flask
C
7.8.1
Leach soil from Step 7.5 with acidified NaCl
7.8.2
Transfer leachate to Kjeldahl flask; add NaOH; distill into H_3BO_3 sol.
D


C
D
7.7.3 Add Na_2CO_3 solution and paraffin oil: attach flask to apparatus
7.7.4 Aerate for 17 hours
7.7.5 Shut off suction: remove flask: titrate residual acid
7.7.5 Calculate content of absorbed ammonium
7.8.3 Titrate H_3BO_3 solution with H_2SO_4
7.8.3 Run blanks: correct titration figure for blanks:
7.8.3 Calculate ammonium in soil
Stop

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Contamination From Battery Salvage Operations On The Chipola River, Florida

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Abstract: Trace elements (As, Cd, Cr, Cu, Hg, Pb, Se, and Zn) were measured in fish, clams, and sediment in 1982 to determine whether the effluents from 2 abandoned battery salvage operations were contaminating the Chipola River, Florida. Concentrations of the metals were generally low, but tended to increase downstream from past sites. Elevated concentrations may reflect residual contamination from the battery salvage operations as well as increased land-use development and proximity to major highways. Concentrations of trace elements in samples of biota and sediment demonstrated no serious contaminant problem in the Chipola River.

Proc. Annu. Conf. Southeast. Assoc. Fish and Wildl. Agencies 38:139–145

Possible contamination of the Chipola River from 2 abandoned battery salvage companies has caused concern for downstream fish and wildlife resources of the Apalachicola River and Estuary in northwest Florida. High levels of metals, sulfate, and acidity were found in drainage water and sediments in 1981 by the Florida Department of Environmental Regulation (unpubl. data) during a preliminary survey of the plant sites. Old batteries were cut open and drained, and the lead was recovered for resale during operation of these facilities. Contaminants associated with these operations were sulfuric acid (H_2SO_4), sulfate, and the metals Cd, Cu, Pb, Ni and Zn. Concentrations of Al and Mn were also high in these areas, but these metals occurred naturally and were leached from the soil under the acidic condition caused by H_2SO_4. At a battery salvage plant that operated from 1970 to 1980, north of Alford, Florida, effluents containing H_2SO_4 and associated metals drained directly into a swamp, killing the vegetation there before they entered Dry Creek, which

DETERMINATION OF TOXIC ELEMENTS

The method described is appropriate for the determination of antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc in biological tissues. Acid digestion procedures as described in EPA CLP (7000 series) are appropriate for the method. Monitoring of instrument and method performance, initial and on-going calibration, and quality assurance and quality control monitoring of data, should be performed as stated in EPA CLP.

Method Summary

Five grams of tissue is homogenized, subsampled, and digested using wet oxidation methods. Elemental determinations are made utilizing the appropriate instrumentation as recommended in EPA CLP, as are method performance parameters.

Sample Collection, Preservation, and Storage

Sample handling, preparation and storage after collection should follow the recommendation previously described for determination of organic compounds in biological tissue. Storage times and conditions consistent with those stated in EPA CLP for the determination of metals in water samples would be appropriate for extracted samples.

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ows 16 km to the Chipola River. This plant processed more than 50,000 batteries er week during peak operation. Another battery salvage company, which operated n 1979-1982, was about 3 km from the Chipola River and 3 km upstream from its nfluence with Dry Creek. Contaminated material from this site entered the Chipola River by way of groundwater and surface runoff from unlined holding onds constructed in porous sand.

The Chipola River originates in Alabama below Dothan and flows southward hrough Jackson, Calhoun, and Gulf counties, Florida, before draining into the Apalachicola River at about river mile 27. These river systems are an integral part f one of the few relatively undisturbed bottomland hardwood swamps and estuaries f the United States. Freshwater and estuarine resources associated with this system re recreationally and commercially important and contribute significantly to the conomy of northwest Florida. The area is comparatively pristine; however, some gricultural developments and small towns are present in the drainage, especially in he central portion.

Contamination with metals is of particular importance to ecological systems ecause of their toxicity and their persistence in the environment (Mielinen 1977). Metals remain available for uptake, transportation, and transformation for a long ime because of their inorganic properties (Hoover 1978). Uptake and accumulation f metals by biota vary with biotic species, metal, and water chemistry, but levels bove background concentrations generally indicate contamination from anthropoenic sources. The objective of this study was to determine if toxic trace elements metals) associated with battery salvage operations were present in sediments and iota of the Chipola River.

This study was financed by the U.S. Department of the Interior, Fish and Wildlife Service, Region IV, Atlanta, Georgia. The authors thank Lorna Sicarello, Jim Barkuloo, Pledger Moon, Jay Troxel and personnel from the Florida Game and Freshwater Fish Commission for their assistance in making field collections.

Methods

Ten study sites were established along the Chipola River to assess the possible contamination contributed from the battery salvage plants. Stations 1 and 2 were bove the discharge areas, stations 3 and 4 in potential discharge areas, and stations 5-10 were distributed below them; stations 8 and 9 were in Dead Lake, a small reservoir near the lower end of the river. Both Interstate Hwy. 10 and U.S. Hwy. 90 ross the Chipola River in the vicinity of station 3.

Samples of largemouth bass (*Micropterus salmoides*), spotted sucker (*Minytrema melanops*), Asiatic clam (*Corbicula manilensis*), and sediment were collected rom 10 locations in the Chipola River in September 1982. Three composite samples f 5 fish each and 3 samples of clams and sediment were obtained from each station. ish were collected by electrofishing and were weighed and measured. Tissues were xtracted from the shells of clams hand-collected from the stream bottom, combined into a sample, and weighed. Individual fish and composite samples of clams

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were wrapped in aluminum foil. Sediment samples were collected using an Ekman grab; each sample consisted of a subsample from 3 grab samples. Sediment samples were stored in linear polyethylene bags. All samples were placed on ice after collection and frozen as soon as possible (nearly always within 8 hours).

Samples were analyzed for organochlorine insecticides and 8 potentially toxic trace elements (As, Cd, Cr, Cu, Hg, Pb, Se, and Zn). Residue analyses were conducted on whole fish. Samples were homogenized in a Hobart® food grinder. For organochlorine analysis, a 25-g subsample was mixed with sodium sulfate and then petroleum ether for extraction. Florisil was used to clean up the extract in part, and silica gel for additional cleanup. Measurements were made with a gas chromatograph equipped with an electron capture detector.

Samples for Cd, Cr, Cu, Pb, Hg, and Zn analysis were prepared by refluxing with nitric acid. Samples for As and Se determinations were digested with a nitric-perchloric acid mixture. Using atomic absorption spectroscopy techniques, As and Se were analyzed by hydride generation, Hg by a cold-vapor technique, and a graphite furnace was used for Cd, Cr, and Pb. Cu and Zn were determined by inductively coupled argon plasma emission spectroscopy.

Analysis of variance and Duncan's multiple range test, available on the Statistical Analysis System (Helwig and Council 1982) at the University of Georgia computer center, were used to analyze transformed data ($\log x + 1$) by species among stations.

Results and Discussion

Metal concentrations in sediments and biota of the Chipola River were not considered excessively high, but levels generally increased downstream from the background levels at the 2 upstream stations (Table 1). The downstream increase of As, Cd, Cr, Pb, and Zn was particularly noticeable in clam and sediment samples. Elevated levels may reflect residual contamination from the abandoned battery salvage operations as well as increased land-use developments (agriculture and urbanization) and proximity to highways, which has been shown to cause significant increases in metal levels (Von Hassel et al. 1980).

Concentrations of As, Cd, and Se in fish from the Chipola River were similar to those measured in biota from the Apalachicola River (Winger et al. 1984). Pb levels in clams were higher in the Chipola River than reported in the Apalachicola River. Concentrations of Hg in largemouth bass and spotted suckers from the Chipola River were <0.5 ppm, the concentration generally accepted as natural in unpolluted environments (Abernathy and Cumbie 1977), and substantially less than the 1 ppm (methyl mercury) action level allowed in fish for human consumption (U.S. Food and Drug Adm. 1984).

The higher concentrations of As in *Corbicula* than in fish demonstrated that As bioaccumulates in this mollusk, but does not biomagnify. Arsenic is generally accu-

Reference to trade names or manufacturers does not imply U.S. Government endorsement of commercial products.

Table 1. Organochlorine and metal residues (ppm whole body, wet weight) in biota and sediment from the Chipola River, Florida, 1982.[1]

Sample and Station	Average weight (g)	Lipid (%)	Organochlorines			Metals							
			Total DDT	PCB	Other[2] Organic	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
Largemouth bass (N=3 composite samples of 5 fish each)													
1	194	2.53[abc]	0.07[ef]	ND[d]	ND[c]	0.05[c]	0.04[c]	0.47[bc]	0.78[c]	0.48[c]	0.07[c]	0.40[abc]	13.98[abc]
2	241	1.64[bc]	0.04[f]	ND[d]	ND[c]	0.05[c]	0.04[c]	0.32[d]	0.71[c]	0.46[c]	0.05[c]	0.46[abc]	11.59[bc]
3	446	1.21[c]	0.14[cd]	0.20[b]	0.03[b]	0.05[c]	0.17[b]	0.59[b]	0.81[c]	0.38[c]	0.06[c]	0.51[ab]	15.65[b]
4	320	1.31[bc]	0.06[ef]	0.08[bcd]	0.01[c]	0.06[c]	0.04[c]	0.54[ab]	0.74[c]	0.28[c]	0.09[c]	0.53[a]	16.23[b]
5	333	1.93[abc]	0.05[f]	0.03[cd]	0.01[c]	0.05[c]	0.05[c]	0.46[bc]	0.53[c]	0.25[c]	0.05[c]	0.41[abc]	14.65[b]
6	425	3.21[a]	0.10[def]	0.04[cd]	0.01[c]	0.05[c]	0.09[c]	0.42[c]	0.54[c]	0.38[c]	0.08[c]	0.50[ab]	14.32[b]
7	406	2.73[ab]	0.07[ef]	ND[d]	0.01[c]	0.05[c]	0.19[b]	0.47[bc]	0.52[c]	0.43[c]	0.07[c]	0.38[bc]	13.93[bc]
8	503	3.34[a]	0.13[cde]	0.13[bc]	0.03[b]	0.07[c]	0.05[c]	0.49[abc]	0.89[c]	0.33[c]	0.43[b]	0.33[c]	15.17[b]
9	462	2.18[abc]	0.08[def]	0.07[bcd]	0.01[c]	0.09[c]	0.17[b]	0.59[b]	0.65[c]	0.37[c]	0.05[c]	0.39[abc]	15.67[b]
10	638	6.61[a]	0.13[c]	0.14[bc]	ND[c]	0.05[c]	0.05[c]	0.48[abc]	0.73[c]	0.42[c]	0.11[c]	0.50[ab]	14.14[bc]
Spotted sucker (N=3 composite samples of 5 fish each)													
1	394	6.48[a]	0.09[def]	ND	ND[c]	0.06[c]	0.07[c]	0.33[d]	0.71[c]	0.15[c]	0.05[c]	0.50[abc]	15.42[b]
2	532	4.08[abc]	0.05[ef]	ND	0.03[b]	0.07[c]	0.07[c]	0.37[cd]	0.66[c]	0.21[c]	0.08[c]	0.77[a]	16.50[ab]
3	449	3.89[abc]	0.09[def]	0.17[b]	0.06[a]	0.06[c]	0.04[c]	0.41[cd]	0.74[c]	0.10[c]	0.17[c]	0.51[abc]	17.15[ab]
4	467	3.34[abc]	0.13[c]	0.14[bc]	0.04[ab]	0.06[c]	0.09[c]	0.57[b]	3.13[b]	0.38[c]	0.31[c]	0.61[ab]	20.24[a]
5	472	3.74[abc]	0.08[def]	ND	0.03[b]	0.11[c]	0.07[c]	0.46[bc]	0.64[c]	0.11[c]	0.08[c]	0.53[abc]	17.17[ab]
6	588	4.12[ab]	0.11[cd]	ND	0.04[ab]	0.08[c]	0.05[c]	0.35[d]	0.86[c]	0.17[c]	0.10[c]	0.42[abc]	16.67[ab]
7	654	4.22[ab]	0.04[f]	ND	ND[c]	0.07[c]	0.18[b]	0.55[b]	7.56[a]	0.13[c]	0.88[b]	0.51[abc]	19.65[a]
8	642	6.03[a]	0.06[def]	ND	0.01[c]	0.06[c]	0.05[c]	0.44[bcd]	0.77[c]	0.11[c]	0.05[c]	0.34[c]	17.66[ab]
9	497	5.31[ab]	0.04[f]	ND	ND[c]	0.06[c]	0.05[c]	0.49[abc]	0.88[c]	0.11[c]	0.05[c]	0.39[abc]	20.05[a]
10	433	10.90[a]	0.12[c]	0.16[b]	0.02[b]	0.05[c]	0.05[c]	0.44[bcd]	0.88[c]	0.13[c]	0.07[c]	0.39[abc]	15.69[b]
Asiatic clam													
1	91[1(142)][4]	1.17[c]	0.01[f]	ND	ND	0.28[f]	0.42[ab]	1.09[ab]	6.74[a]	0.18[abc]	0.27[b]	NA	23.35[b]
2	80(164)	1.14[c]	0.01[f]	ND	ND	0.63[ab]	0.50[ab]	1.86[abc]	10.73[a]	0.18[abc]	0.28[b]	NA	22.76[b]
3	161(209)	1.33[c]	0.01[f]	ND	ND	0.55[ab]	0.22[c]	2.81[a]	8.17[a]	0.08[c]	0.46[b]	0.81[a]	23.00[b]
4	95(199)	1.24[c]	0.01[f]	ND	ND	0.94[abc]	0.44[ab]	2.31[ab]	13.14[a]	0.09[bc]	0.63[b]	1.02[a]	24.81[b]
5	42(102)	0.64[d]	ND[e]	ND	ND	NA	0.52[a]	2.75[a]	8.83[a]	NA	0.25[b]	NA	20.97[b]
6	80(171)	1.21[c]	0.01[f]	ND	ND	0.77[abc]	0.38[b]	2.04[abc]	19.23[a]	0.19[abc]	1.18[a]	NA	29.89[a]
7	37(42)	1.30[c]	ND[e]	ND	ND	NA	0.47[ab]	1.57[abc]	18.17[a]	NA	1.02[a]	NA	26.39[b]
8	118(110)	1.85[b]	0.01[f]	ND	ND	1.10[abc]	0.27[c]	1.88[abc]	8.30[a]	0.20[bc]	0.41[b]	0.83[a]	21.40[b]
9	127(178)	1.87[b]	0.01[f]	ND	ND	1.37[ab]	0.16[c]	1.20[abc]	12.67[a]	0.13[abc]	0.60[b]	0.65[a]	20.20[b]
10	106(94)	2.49[a]	0.09[def]	ND	ND	1.50[a]	0.23[c]	0.92[c]	8.64[a]	0.08[c]	0.18[b]	0.75[ab]	21.78[b]

Sample and Station	Average weight (g)	Lipid (%)	Organochlorines			Metals							
			Total DDT	PCB	Other[2] Organic	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
Sediment[5] (N=3/station)													
1	100	19.7[a]	ND[e]	ND	ND	0.60[abc]	0.08[c]	6.71[a]	0.65[a]	0.05[a]	2.97[a]	NA	5.57[a]
2	100	24.6	ND[e]	ND	ND	0.77[abc]	0.18[c]	11.09[a]	1.02[a]	0.05[a]	4.32[a]	NA	8.21[a]
3	100	23.8	ND[e]	ND	ND	1.12[ab]	0.17[c]	9.63[a]	1.90[a]	0.05[a]	10.18[a]	NA	15.19[a]
4	100	20.7	ND[e]	ND	ND	0.50[c]	0.14[c]	7.24[a]	0.94[a]	0.05[a]	3.75[a]	NA	9.07[a]
5	100	20.3	ND[e]	ND	ND	0.50[c]	0.12[c]	5.95[a]	0.76[a]	0.05[a]	3.09[a]	NA	7.24[a]
6	100	30.0	ND[e]	ND	ND	1.77[a]	0.28[c]	12.63[a]	2.00[a]	0.05[a]	8.52[a]	NA	16.28[a]
7	100	39.9	ND[e]	ND	ND	0.50[c]	0.27[c]	10.37[a]	1.91[a]	0.05[a]	14.65[a]	NA	19.10[a]
8	100	42.2	0.03[f]	ND	ND	0.82[abc]	0.20[c]	10.28[a]	1.86[a]	0.05[a]	11.47[a]	NA	25.33[a]
9	100	54.4	0.01[f]	ND	ND	1.86[ab]	0.23[c]	18.88[a]	7.69[a]	0.06[a]	13.37[a]	NA	35.13[a]
10	100	30.3	ND[e]	ND	ND	2.00[a]	0.09[c]	14.51[a]	4.84[a]	0.05[a]	9.93[a]	NA	26.76[a]

NOTE: ND = not detected
NA = not analyzed
[1]Values with the same superscript within a column and sample group are not significantly different (P<0.05)
[2]α BHC, mirex, dieldrin, aldrin, α chlordane, γ chlordane
[3]Mean weight of sample
[4]Mean number of Asiatic clams excluding shell
[5]Mean percentage moisture
[6]Concentrations in sediments expressed on a wet-weight basis

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